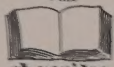




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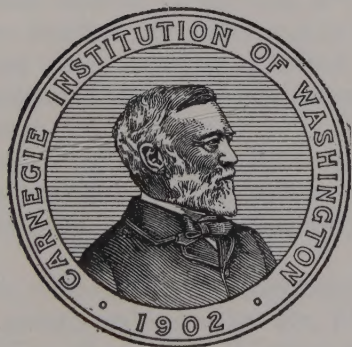
I. U. SCHOOL OF MEDICINE

CONDUCTIVITIES AND VISCOSITIES IN PURE AND IN MIXED SOLVENTS

RADIOMETRIC MEASUREMENTS OF THE IONIZATION CONSTANTS OF INDICATORS, ETC.

BY

HARRY C. JONES AND COLLABORATORS



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PREFACE.

The investigations discussed in this monograph might seem, at first sight, to deal with a variety of subjects, some of which have no very close relation to the others; but nearly all of these lines of work were suggested by the solvate theory of solution as proposed here about fifteen years ago, and have been carried out with the specific purpose of ascertaining their bearing on this theory.

Dr. Davis studied the viscosities of solutions of cæsium salts in mixed solvents, and in mixtures of the associated liquids water, formic acid, and acetic acid, in its relation to the theory of viscosity proposed by Jones several years ago.

Dr. Davis and Dr. Putnam investigated the dissociating power of formamid as a solvent, in connection with its bearing on a theory of the relation between the dissociating power of a solvent and other physical properties of that liquid; namely, its dielectric constant and its own association.

Dr. Shaeffer and Dr. Paulus used the new spectroscope constructed to study the nature of "solvent bands," to determine the constants of indicators—a quantity absolutely essential to the scientific use of these substances in quantitative analysis.

This work was extended by Dr. Paulus and Mr. Hutchinson to the indicator, corallin.

Having found such a marked difference between the physical behavior towards light of free and of combined water, Dr. J. E. L. Holmes took up the study of a reaction effected by the ions of water—the saponification of an ester—to see whether any difference in the chemical activity of free and of combined water could be detected. It seems that such a difference exists, combined water having apparently greater chemical activity than free water.

This work was extended by Mr. Connolly to another reaction which proceeds much more rapidly—the hydration of acetic anhydride. This work has not yet been extended sufficiently to justify any final conclusion.

The work begun two years ago on the conductivities of organic acids in ethyl alcohol, was greatly extended by Dr. Lloyd and Mr. Wiesel, comprising the study of nearly forty of the more common organic acids in this solvent. The aim of this work is to arrive at a knowledge of the dissociation of these substances by alcohol, and the degree of solvation of these compounds in alcohol.

Dr. Watkins has extended work begun in this laboratory about a dozen years ago on the conductivity and dissociation of salts by water. He has studied a number of the less common salts, and has obtained very accurate results which, in general, confirm the conclusions drawn from our earlier work in this field.

The different physical behavior of free and of combined water suggested to Dr. Shaeffer the desirability of studying the relative dissociating powers of free and of combined water. This work was undertaken by Mr. Ordeman. He prepared isochloric solutions of the slightly hydrated salt potassium chloride, and of the strongly hydrated salt calcium chloride, and used these solutions as solvents in which to dissolve chlorides and measure their dissociations. The dissociation of a number of salts in these solvents was measured; and while we are not yet prepared to draw any final conclusions, it seems probable that "combined" water has rather less dissociating power than "free" water.

The absorption and adsorption of the slightly hydrated salt potassium chloride by soils, is a problem of both scientific and technical importance. Work has been in progress in my laboratory on this problem during the past year by Mr. McCall, with the cooperation of Messrs. Hildebrandt, Johnston, F. S. Holmes, and Trelease. They find that a part of the potassium chloride is absorbed or combined chemically with the soil particles, and a part is adsorbed or in a state of physical union with the particles of the soil. Under certain conditions the solvent may be more rapidly adsorbed than the salt.

The results of these investigations, many of which have been carried out with the aid of grants generously awarded me by the Carnegie Institution of Washington, are all recorded in this publication.

HARRY C. JONES.

JOHNS HOPKINS UNIVERSITY,
June, 1915.

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IN MIXED SOLVENTS

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CONSTANTS OF INDICATORS

BY

HARRY C. JONES AND COLLABORATORS

CHAPTER I.

THE VISCOSITIES OF SOLUTIONS OF CÆSIUM SALTS IN MIXED SOLVENTS; THE VISCOSITIES OF BINARY MIXTURES OF THE ASSOCIATED LIQUIDS, WATER, FORMIC ACID, AND ACETIC ACID; TOGETHER WITH SOME NEW FORMS OF APPARATUS.

BY P. B. DAVIS.

INTRODUCTION.

We have endeavored for some time to secure enough cæsium salts to study their viscosities in pure and in mixed solvents, but only within the past year have we been successful. Through the courtesy and cooperation of Professor James Lewis Howe of Washington and Lee University, a quantity of cæsium sulphate was placed at our disposal. This was converted first into the hydroxide, then into the carbonate, and finally into the chloride and nitrate; and with these salts this investigation has been carried out.

Cæsium is the most electro-positive of all the elements, and is further distinguished by possessing the largest atomic volume, being followed in this respect by rubidium and potassium, respectively. Since salts of the latter two elements are of great interest from the viscosity standpoint, it would be expected that cæsium salts would possess, to a much more pronounced degree, any peculiarities shown by salts of rubidium and potassium.

An examination of the literature bearing on viscosity shows that, in general, only the salts of the three metals mentioned above are known to lower the viscosity of water. The effect of potassium and rubidium salts on the viscosities of solvents other than water, and of mixtures of such solvents with one another and with water, has been the subject of earlier investigations in this laboratory; and this series of investigations can now be regarded as partially completed by this study of cæsium salts in these solvents. The present investigation, therefore, has been made to comprise a study of the viscosities of the two cæsium salts, chloride and nitrate, in water and in binary mixtures of methyl alcohol, ethyl alcohol, and acetone with water.

The results obtained with these salts of cæsium in formamid as a solvent are published in Chapter II, and further determinations of their behavior in glycerol and glycerol-water mixtures, as well as in mixed solvents containing formamid instead of water are now in progress.

HISTORICAL.

Jones and Lindsay, in their work on binary mixtures of the alcohols with water, found that the molecular conductivities of solutions of salts in these solvents were in every case less than the averages calculated from the conductivities in the component solvents themselves. These

results, interpreted in the light of the work of Dutoit and Aston, point to a lower degree of association in the case of the mixed solvents than in that of the pure solvents themselves. That this is true was shown by Jones and Murray, who carried out cryoscopic measurements with mixtures of water, formic acid, and acetic acid; and showed that the molecular weights of these substances were always less in solution than the molecular weights of the pure solvents themselves, as determined by the method of Ramsay and Shields.

Jones and Carroll, in extending this investigation, showed that the change in the viscosity of the medium was an important factor conditioning the decrease in the conductivity of salts in such binary mixtures of liquids, the decrease in ionization due to changes in association being only one of the factors to be taken into account.

However, it remained for Jones and Veazey to offer a satisfactory explanation of the increase in viscosity which occurs when two highly associated liquids are mixed, and also to account for the phenomenon of negative viscosity, or the lowering of the viscosity of the solvent by a dissolved substance. They carried out an extensive investigation in mixtures of the alcohols and of acetone with water, and found that the conductivity minima referred to above were more general than had hitherto been supposed, and that this was very closely related to the fluidity minima observed in these same mixtures.

The work of Thorpe and Rodger having shown that viscosities depend largely upon the frictional surfaces of the physical particles in any solution, it followed that if these surfaces were increased or diminished by any means whatsoever, there would result a corresponding increase or decrease in the fluidity of the medium. The work of Jones and Murray, as already stated, had brought out the fact that on mixing two highly associated liquids a material diminution in the association of both takes place. This would result in an increase in the number of ultimate particles in a given volume, with a corresponding decrease in their size, and therefore an increase in their frictional surfaces which would be exposed to one another. Consequently, the viscosity curves for the various mixtures should pass through a maximum, the position of which would depend upon the relative effects of the solvents upon one another.

Quite recently Jones and Davis, studying viscosity, tested the results obtained by Jones and Murray, using the same mixtures which they had employed—acetic acid and water, formic acid and water, and formic acid and acetic acid. They obtained results, recorded later in this chapter, which were in perfect accord with the earlier work of Jones and Murray. It was shown that the curve for the viscosity of acetic acid and water passes through a well-defined maximum towards the acetic acid end of the curve, showing the large effect of water on the association of acetic acid; while the curve for formic acid and acetic

acid exhibited only a slight maximum near its center, which showed that the two liquids possessed about the same small effect, each on the association of the other. On the other hand, the curve for formic acid and water was practically a straight line, indicating that neither solvent altered appreciably the association of the other.

The reason for the maximum in such viscosity curves and their relation to conductivity having been explained, the effect of certain salts in lowering the viscosity of the solvent remained to be interpreted. Potassium, rubidium, and cæsium salts, as has already been stated, were known to lower the viscosity of water. These elements occupy the highest maxima on the atomic volume curve and, as Wagner has shown, they possess negative viscosity coefficients in water which vary directly as their volumes. The explanation offered by Jones and Veazey to account for these facts was that salts of these metals lower the viscosity of the solvent by introducing into it ions which are so large that when mixed with the molecules of the solvent they lower the total frictional surfaces exposed to one another. That certain salts of potassium do not produce this effect is due to the fact that the viscosity of the solution is also a function of the anions as well as of the cations. When the volume of the anion is very small, the negative effect of the cation on the viscosity of the solution is more than overcome, and positive viscosity results.

Applying this hypothesis of Jones and Veazey to mixed solvents, Jones and his co-workers have been able to explain a number of facts which otherwise appear to be inexplicable. For example, it has been found that rubidium halides and potassium iodide lower the viscosity of binary mixtures of the alcohols and of acetone with water which contain as much as 50 per cent water; while the corresponding increase in viscosity takes place in all mixtures containing the larger percentage of alcohol. The explanation of this fact follows at once from what has been stated above. These salts lower the viscosity of water and increase the viscosity of the other solvents in which they dissolve. On mixing the two, as soon as the association of the alcohol is sufficiently diminished so that the solvent aggregates become smaller than the particles of the dissolved substances, the total frictional surface between the two becomes less and negative viscosity results.

In glycerol as a solvent, not only were rubidium salts and some potassium salts found to lower the viscosity of the solvent, but also certain of the ammonium salts. So great was the negative viscosity effect produced by concentrated solutions of rubidium salts, that an increase in the conductivity of these solutions over that of the more dilute solutions was noted, although the ionization of the more dilute solutions was undoubtedly greater than that of the more concentrated. Ammonium salts were found to be more closely allied to salts of rubidium than to those of potassium, in respect to their effect on viscosity.

The explanation of the above phenomena observed by Jones and his co-workers follows directly from and substantiates the suggestion made by Jones and Veazey.

APPARATUS AND PROCEDURE.

In carrying out this investigation, the same viscosity apparatus was used as in our work with formamid as a solvent, recorded in Chapter II of this monograph. The scheme of temperature regulation and the methods of obtaining the results were also identical with those used in that work.

The cæsium salts were all carefully recrystallized and dried at 135° before using.

The mixed solvents were made up by volume at 20°, from liquids purified by the usual methods, and all solutions in these liquids were prepared at the same temperature.

TABLE 1.—*Viscosity and Fluidity of Cæsium Salts in Mixtures of Water with Methyl Alcohol, Ethyl Alcohol, and Acetone at 15°, 25°, and 35°.*

	Mol. conc.	Viscosities.			Fluidities.		
		η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°
<i>Cæsium Chloride</i> in 75 p. ct. Methyl Alcohol with Water.	0.50	0.01674	0.01309	0.01049	59.74	76.39	95.33
	0.25	0.01637	0.01275	0.01021	61.09	78.43	97.94
	0.10	0.01613	0.01243	0.00997	62.00	80.45	100.30
	Solv.	0.01594	0.01235	0.01032	62.75	80.97	96.90
<i>Cæsium Chloride</i> in 50 p. ct. Methyl Alcohol with Water.	0.50	0.02119	0.01547	0.01200	47.19	64.64	83.33
	0.25	0.02084	0.01553	0.01197	47.98	64.39	83.54
	0.10	0.02086	0.01531	0.01179	47.94	65.32	84.82
	Solv.	0.02100	0.01535	0.01169	47.62	65.15	85.54
<i>Cæsium Chloride</i> in 25 p. ct. Methyl Alcohol with Water.	0.50	0.01778	0.01338	0.01048	59.74	76.39	95.33
	0.25	0.01828	0.01360	0.01047	61.09	78.43	97.94
	0.10	0.01862	0.01358	0.01044	62.00	80.45	100.34
	Solv.	0.01871	0.01359	0.01032	62.74	80.97	102.23
<i>Cæsium Chloride</i> in Water.	2	0.01098	0.00877	0.0713	91.07	114.03	140.25
	4	0.01111	0.00889	0.0716	90.01	112.48	139.66
	10	0.01133	0.00884	0.0719	88.18	113.12	139.08
	Solv.	0.01134	0.00891	0.0721	88.18	112.23	138.89
<i>Cæsium Nitrate</i> in 75 p. ct. Methyl Alcohol with Water.	2						
	4						
	10		0.01244	0.00987		80.39	101.27
	Solv.	0.01594	0.01235	0.00978	62.74	80.97	102.23
<i>Cæsium Nitrate</i> in 50 p. ct. Methyl Alcohol with Water.	2						
	4		0.01520	0.01177		65.83	84.96
	10	0.02072	0.01543	0.01182	48.26	64.81	84.60
	Solv.	0.02100	0.01535	0.01169	47.62	65.15	85.54
<i>Cæsium Nitrate</i> in 25 p. ct. Methyl Alcohol with Water.	2		0.01300	0.01018		76.92	98.23
	4	0.01795	0.01331	0.01028	55.71	75.13	97.28
	10	0.01832	0.01346	0.01031	54.59	74.29	96.99
	Solv.	0.01871	0.01359	0.01032	53.45	73.45	96.90

TABLE 1.—Viscosity and Fluidity of Cæsium Salts in Mixtures of Water with Methyl Alcohol, Ethyl Alcohol, and Acetone at 15°, 25°, and 35°—Continued.

	Mol. conc.	Viscosities.			Fluidities.		
		η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°
<i>Cæsium Nitrate</i> in Water...	2	0.01075	0.00858	0.00703	93.02	116.55	142.25
	4	0.01102	0.00871	0.00705	90.74	114.81	141.84
	10	0.01122	0.00885	0.00720	89.13	112.99	138.89
	Solv.	0.01134	0.00891	0.00720	88.18	112.23	138.89
<i>Cæsium Chloride</i> in 75 p. ct. Ethyl Alcohol with Water.	2	0.02777	0.02061	0.01590	36.01	48.52	62.89
	4	0.02783	0.02039	0.01561	35.93	49.04	64.06
	10	0.02761	0.01994	0.01500	36.22	50.15	66.67
	Solv.	0.02762	0.01997	0.01537	35.21	50.08	65.06
<i>Cæsium Chloride</i> in 50 p. ct. Ethyl Alcohol with Water.	2	0.03176	0.02245	0.01635	31.49	44.54	61.16
	4	0.03346	0.02283	0.01666	29.89	43.80	60.02
	10	0.03359	0.02274	0.01648	29.77	43.98	60.68
	Solv.	0.03400	0.02286	0.01618	29.41	43.73	61.80
<i>Cæsium Chloride</i> in 25 p. ct. Ethyl Alcohol with Water.	2	0.02381	0.01694	0.01262	42.00	59.03	79.24
	4	0.02472	0.01738	0.01282	40.45	57.54	78.00
	10	0.02522	0.01736	0.01276	39.65	57.60	78.37
	Solv.	0.02585	0.01760	0.01270	38.68	56.82	78.74
<i>Cæsium Chloride</i> in Water...	2	0.01098	0.0877	0.0713	91.07	114.03	140.25
	4	0.01111	0.0889	0.0716	90.01	112.48	139.66
	10	0.01133	0.0884	0.0719	88.18	113.12	139.08
	Solv.	0.01134	0.0891	0.0720	88.18	112.23	138.89
<i>Cæsium Nitrate</i> in 75 p. ct. Ethyl Alcohol with Water.	2	Insol- uble.					
	4						
	10						
	Solv.						
<i>Cæsium Nitrate</i> in 50 p. ct. Ethyl Alcohol with Water.	2						
	4						
	10						
	Solv.						
<i>Cæsium Nitrate</i> in 25 p. ct. Ethyl Alcohol with Water.	2						
	4	0.02424	0.01697	0.01261	41.25	58.93	79.37
	10	0.02526	0.01745	0.01276	39.59	57.31	78.37
	Solv.	0.02585	0.01760	0.01270	38.68	56.82	78.74
<i>Cæsium Nitrate</i> in Water...	2	0.01075	0.00858	0.00703	93.02	116.55	142.25
	4	0.01102	0.00871	0.00705	90.74	114.81	141.84
	10	0.01122	0.00885	0.00720	89.13	112.99	138.89
	Solv.	0.01134	0.00891	0.00720	88.18	112.23	138.89
<i>Cæsium Chloride</i> in 75 p. ct. Acetone with Water.	2						
	4	0.01188	0.00930	0.00764	84.18	107.52	130.89
	10	0.01135	0.00904	0.00740	88.11	110.56	135.08
	Solv.	0.01125	0.00896	0.00732	88.88	111.66	136.59
<i>Cæsium Chloride</i> in 50 p. ct. Acetone with Water.	2	0.01785	0.01354	0.01060	56.02	73.86	94.34
	4	0.01783	0.01337	0.01038	56.09	74.79	96.34
	10	0.01777	0.01316	0.01029	56.27	76.05	97.18
	Solv.	0.01766	0.01306	0.01009	56.63	76.57	99.11
<i>Cæsium Chloride</i> in 25 p. ct. Acetone with Water.	2	0.01647	0.01250	0.00983	60.72	80.00	101.71
	4	0.01667	0.01254	0.00979	59.99	79.74	102.10
	10	0.01677	0.01246	0.00978	59.63	80.26	102.26
	Solv.	0.01690	0.01248	0.00964	59.17	80.12	103.78

TABLE 1.—*Viscosity and Fluidity of Cæsium Salts in Mixtures of Water with Methyl Alcohol, Ethyl Alcohol, and Acetone at 15°, 20°, and 35°—Continued.*

	Mol. conc.	Viscosities.			Fluidities.		
		η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°
<i>Cæsium Chloride</i> in Water..	2	0.01098	0.00877	0.0713	91.07	114.03	140.25
	4	0.01111	0.00889	0.0716	90.01	112.48	139.66
	10	0.01133	0.00884	0.0719	88.18	113.12	139.08
	Solv.	0.01134	0.00891	0.0720	88.18	112.23	138.89
<i>Cæsium Nitrate</i> in 75 p. ct. Acetone with Water.	2						
	4						
	10	0.01143	0.00904	0.00737	87.48	110.62	135.76
	Solv.	0.01119	0.00878	0.00680	89.37	113.90	147.12
<i>Cæsium Nitrate</i> in 50 p. ct. Acetone with Water.	2						
	4	0.01759	0.01320	0.01030	56.85	75.76	97.09
	10	0.01756	0.01307	0.01017	56.95	76.45	98.33
	Solv.	0.01767	0.01304	0.01007	56.59	76.69	99.30
<i>Cæsium Nitrate</i> in 25 p. ct. Acetone with Water.	2	0.01610	0.01216	0.00965	62.11	82.84	103.63
	4	0.01655	0.01229	0.00971	60.42	81.37	103.02
	10	0.01665	0.01244	0.00968	60.06	80.39	103.35
	Solv.	0.01673	0.01232	0.00962	59.77	81.18	102.00
<i>Cæsium Nitrate</i> in Water...	2	0.01075	0.00858	0.00703	93.02	116.55	142.25
	4	0.01102	0.00871	0.00705	90.74	114.81	141.84
	10	0.01122	0.00885	0.00720	89.13	112.99	138.89
	Solv.	0.01134	0.00891	0.00720	88.18	112.23	138.89

DISCUSSION OF RESULTS.

As can be seen from table 1, measurements have been made of the viscosities of solutions of these salts at 15°, 25°, 35° in mixtures of 25, 50, and 75 per cent of each of the three solvents with water. Cæsium salts, with the possible exception of the carbonate, are practically insoluble in the alcohols and in acetone; and in a number of cases it was impossible to obtain solutions more concentrated than one-fourth normal in the 75 per cent mixtures. In fact, cæsium nitrate was not more soluble than tenth-normal in 75 per cent methyl alcohol and 75 per cent acetone, while it is impossible to obtain even that concentration in 75 per cent ethyl alcohol. One peculiarity previously noted in the case of rubidium chloride in 75 per cent acetone was also observed with cæsium chloride. A one-half normal concentration of this salt could easily be prepared, but with a partial separation of the acetone from the solvent. However, on cooling below 10° a perfectly homogeneous mixture again resulted, which separated again into two layers on warming. The nitrate at this concentration merely remained partially undissolved. The results obtained are tabulated for each salt under the heads of the different solvent mixtures, the blank spaces indicating that the salt was insoluble at the concentration in question. In general, both of the salts lower the viscosity of water and of the 25 per cent mixture of all the solvents, and increase the viscosity

of the 75 per cent mixture. These facts are in perfect accord with the results obtained in earlier work with salts of potassium and rubidium. In the 50 per cent mixtures the two salts manifest somewhat different behavior. The chloride in 50 per cent methyl alcohol shows an increase in viscosity at all temperatures for the most dilute solutions, and a tendency of the more concentrated solutions to pass over into negative viscosity. The nitrate in the same solvent showed a decided negative viscosity effect.

In 50 per cent ethyl alcohol a decrease in the viscosity of the solutions as compared with that of the solvent was noted at the lower temperature, a transition to positive viscosity taking place at higher temperatures. Again, the nitrate decreases the viscosity of the solvent at all temperatures.

With regard to the 50 per cent acetone-water mixture, an increase in viscosity at all temperatures is to be noted in the case of the chloride, while the nitrate in 50 per cent shows a tendency to decrease the viscosity of the solvent, although it increases it at the higher temperatures. The difference in the effect produced by these salts, in comparison with that produced by the salts of rubidium, lies in the shifting of the transition-point from negative to positive viscosity towards the mixtures containing the larger percentage of acetone. This follows from the different molecular volumes of the cations of rubidium and cæsium. When acetone and water are mixed the principal changes take place in the association of the acetone. Consequently, until considerable water has been introduced the solvent particles are quite large, so that even cæsium nitrate having the largest negative viscosity coefficient in water increases the viscosity of the 75 per cent mixture and even of the 50 per cent mixture, except at lower temperatures. For rubidium salts, no examples of negative viscosity are to be noted until the 37.5 per cent mixture is reached. No data are available for comparison with rubidium salts in alcohol-water mixtures, but it has been shown that potassium iodide increases the viscosity of these mixtures to that concentration containing 40 per cent alcohol. But in this instance, cæsium nitrate decreases the viscosity of the 50 per cent mixture, positive viscosity manifesting itself only in the 75 per cent mixture.

This shifting of the transition-point from negative to positive viscosity towards the more concentrated solvents (regarding water as the diluent), with increase in the molecular volume of the salt, brings out clearly the gradual breaking-down of the associated molecules into smaller particles with greater frictional surfaces; the difference in the sizes of the particles at different points on the dilution curve is clearly seen from the effect produced by salts of different molecular volumes.

The apparent transition from negative to positive viscosity with rise in temperature, noted in certain instances, would seem to indicate either a polymerization of the salt or else a solvent envelope which is

broken up with rise in temperature. Since these salts are the least solvated, the first assumption is apparently the more plausible.

Measurements are now in progress of the effect of these salts on the viscosity of glycerol and of glycerol-water mixtures.

THE VISCOSITIES OF BINARY MIXTURES OF THE ASSOCIATED LIQUIDS, WATER, FORMIC ACID, AND ACETIC ACID.

Jones and Murray¹ showed in 1903 that when two associated liquids are mixed each diminishes the association of the other. They determined the molecular weight of water in formic acid on the one hand and in acetic acid on the other. Also the molecular weight of formic acid in water, and in acetic acid, and finally the molecular weight of acetic acid in water and in formic acid.

They found that the molecular weight of water in formic acid varied from 19.7 at dilution 0.93 N to 21.9 at 6.18 N, showing that the formic acid diminished slightly the association of the water.

The molecular weight of water in acetic acid varied from 21.7 at 0.64 N to 38.8 at 12.65 N. This showed that the acetic acid diminished greatly the association of the water.

The molecular weight of acetic acid in water varied from 55.4 at 0.17 N to 72.1 at 7.06 N, showing that water diminished very appreciably the association of acetic acid.

The molecular weight of acetic acid in formic acid varied from 61.9 at 0.18 N to 83.8 at 9.17 N. The association of the acetic acid was thus diminished considerably by the formic acid.

The molecular weight of formic acid in water varied from 45.2 at 0.38 N to 51.0 at 6.16 N, showing that water had very little effect on the association of the formic acid; and, finally, the molecular weight of formic acid in acetic acid varied from 50.4 at 0.82 N to 65.7 at 8.26 N.

If we take into account the dissociating action of the water on formic and acetic acids, we are justified in concluding that water and formic acid affect each other's association very little; acetic acid and formic acid affect each other's association considerably, while both water and acetic acid have a marked effect each on the association of the other. These facts were used by Jones and Veazey² to explain the increase in viscosity which takes place when water and alcohol are mixed. These are both strongly associated solvents, and each, therefore, very probably diminishes appreciably the association of the other. From a smaller number of larger molecules of each solvent, we have a larger number of smaller molecules of each solvent produced. The surfaces of the molecules present are therefore increased, and, consequently, the friction of these molecules as they move over one another. Viscosity is a function of the surface friction of the molecules.

¹Amer. Chem. Journ., **30**, 193 (1903).

²Zeit. phys. Chem., **61**, 641; **62**, 44 (1908); Carnegie Inst. Wash. Pub. No. **80**, 170 (1907).

In the same manner Jones and Veazey were able to explain why it is that salts of potassium, rubidium, and cæsium lower the viscosity of water and other solvents¹ in which they are dissolved. The large atomic volumes of these cations, when mixed with the molecules of water, diminish the frictional surfaces which come in contact, and, consequently, diminish the viscosity.

Having found the above action of water, formic acid, and acetic acid, each on the association of the other, the question arose, What would be the effect of each on the viscosity of the other? If the above explanations offered by Jones and Veazey were correct, then two liquids, like water and acetic acid, which diminished each other's association, ought to increase the viscosity of one another—the viscosity of the mixture should be greater than that of either pure liquid separately.

The viscosities of binary mixtures of the above-named three liquids were measured at 15° and 25°. Water was regarded as the solvent for formic acid and acetic acid, and solutions of these acids in water were prepared containing by volume 10, 20, 30, 40, 50, 60, 70, 80 and 90 per cent. The acids themselves contained somewhat less than 1 per cent of water. The viscosity and the fluidity (reciprocal of viscosity) data are given in tables 2 to 4.

TABLE 2.—*Viscosities and Fluidities of Formic Acid in Water at 15° and 25°.*

Per cent HCOOH.	η 15°	φ 15°	η 25°	φ 25°
(H ₂ O).....	0.01134	88.18	0.00891	112.23
10.....	0.01215	82.31	0.00932	107.30
20.....	0.01282	78.00	0.01014	98.62
30.....	0.01339	74.68	0.01072	93.28
40.....	0.01408	71.02	0.01135	88.11
50.....	0.01469	68.07	0.01202	83.20
60.....	0.01591	62.85	0.01287	77.70
70.....	0.01693	59.07	0.01371	72.94
80.....	0.01803	55.46	0.01452	68.87
90.....	0.01914	52.25	0.01546	64.68
(HCOOH).....	0.01963	50.94	0.01571	63.65

The viscosity data at 15° are plotted in curves, fig. 1, and the viscosity data at 25° in curves, fig. 2. The viscosities of acetic acid in water pass through a well-defined maximum, which, before we carried out a single measurement of the viscosities of mixtures of these two solvents,² we predicted would be the case from the molecular-weight determinations of this acid in water made by Jones and Murray.

The viscosities of formic acid in acetic acid pass through a slight maximum, as would be expected from the effect of each of these solvents on the molecular weight of the other.

¹Jones and Davis: Zeit. phys. Chem., **81**, 68 (1912); Carn. Inst. Wash. Pub. No. **180**, 179 (1913).

²Since completing our work we find that a few measurements of the viscosities of mixtures of acetic acid in water had been made by Dunstan and Thole: Journ. Chem. Soc., **85**, 825 (1904); **95**, 1560 (1909).

TABLE 3.—Viscosities and Fluidities of Acetic Acid in Water at 15° and 25°.

Per cent CH_3COOH .	η 15°	φ 15°	η 25°	φ 25°
(H_2O) ¹	0.01134	88.18	0.00891	112.23
10.....	0.01368	73.10	0.01059	94.43
20.....	0.01626	61.50	0.01244	80.39
30.....	0.01897	52.72	0.01446	69.16
40.....	0.02143	46.66	0.01624	61.58
50.....	0.02416	41.39	0.01818	55.01
60.....	0.02682	37.29	0.02015	49.63
70.....	0.02935	34.07	0.02219	45.07
80.....	0.03068	32.60	0.02318	43.14
85.....	0.03033	32.90	0.02292	43.63
90.....	0.02786	35.89	0.02115	47.28
95.....	0.02243	44.58	0.01775	56.34
CH_3COOH	0.01410	70.92	0.01174	85.18

¹Values for water taken from Thorpe and Rodger: Phil. Trans., 185A, 449 (1894).

TABLE 4.—Viscosities and Fluidities of Formic Acid in Acetic Acid at 15° and 25°.

Per cent HCOOH .	η 15°	φ 15°	η 25°	φ 25°
(CH_3COOH).....	0.01410	70.92	0.01174	85.18
10.....	0.01558	64.19	0.01286	77.76
20.....	0.01701	58.79	0.01391	71.89
30.....	0.01792	55.80	0.01463	68.36
40.....	0.01883	53.11	0.01506	66.40
50.....	0.01942	51.49	0.01564	63.94
60.....	0.01984	50.40	0.01587	63.01
70.....	0.02012	49.70	0.01607	62.23
80.....	0.02002	49.95	0.01607	62.23
90.....	0.01967	50.84	0.01582	63.21
(HCOOH).....	0.01963	50.94	0.01571	63.65

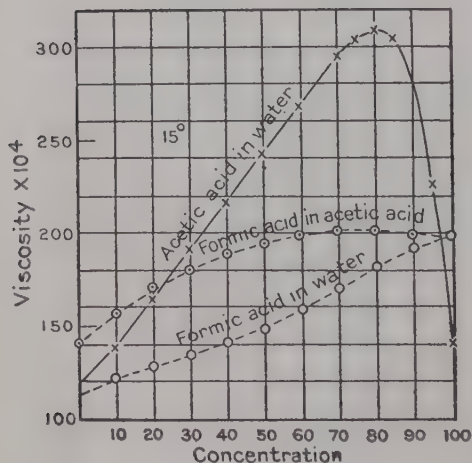


FIG. 1.

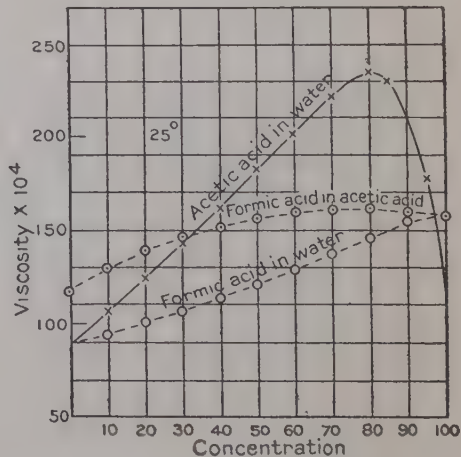


FIG. 2.

The viscosities of mixtures of water and formic acid, on the other hand, fall almost on a straight line. This, again, is just what would be expected, from the fact that neither solvent alters appreciably the molecular weight of the other.

These results are, then, all in keeping with the suggestion made by Jones and Veazey, that the increase in viscosity which results when associated liquids which diminish each other's association are mixed, is due to the *larger number of smaller parts* that are present.

These results are in perfect accord with their suggestion as to the cause of the diminution in the viscosity of water produced by salts whose cations have very large ionic volumes, such as salts of potassium, rubidium, and cæsium.

SOME NEW FORMS OF APPARATUS.

A SUBSTITUTE FOR THE TWIN-BULB TRAP IN TOLUENE-MERCURY THERMO-REGULATORS.

Toluene, on account of its high coefficient of expansion, is to be preferred to all other liquids for use in thermo-regulators. Since, however, it is practically a nonconductor and quite volatile, it is ordinarily used with mercury for the contact in all electrically operated thermostats.

In order to use these two liquids together, the common form of apparatus hitherto employed has been the twin-bulb device, which, however, has the following disadvantages:

1. It is very fragile and can only be made by an expert glass-blower.
2. When the mercury level in the capillary has been once adjusted for any given temperature and the toluene reservoir sealed, the regulator is practically useless for any higher temperatures without opening the reservoir and removing the excess of toluene in order to preserve the equilibrium in the two bulbs.
3. It is difficult to prevent the toluene from finally creeping around between the mercury and the glass walls into the capillary and fouling the contact surface of the mercury, since the same continuous tube contains both the toluene and the mercury.

To overcome these difficulties as far as possible, the apparatus illustrated in figure 3 has been devised. This consists of a bulb *a* attached at the bottom by the tube *b* to the toluene reservoir, which may be of any desired form. Exactly opposite to *b* is a corresponding tube (*c*), which carries the capillary and sealed-in platinum contact.

The interior construction of *a* is as shown in the figure. The small tubes *e* and *f* are prolongations of *c* and *b*, respectively, having a length nearly equal to the diameter of the bulb. These tubes are inclined at an angle of about 30° to the perpendicular. The short side tube *d* is used in filling the regulator and is in exact alinement with *f*.

To prepare the regulator for use, mercury is poured in through the capillary until the bulb *a* is from one-half to three-fourths filled. A

tube drawn out to a small diameter is then inserted through *d* and *f* into *b*, and toluene allowed to run in until the reservoir is filled and also the space in *a* above the mercury. The tube *d* is then sealed, and by adding or withdrawing mercury from the capillary the contact level may be adjusted for any desired temperature.

By this method a toluene-mercury regulator is constructed with a range of 50° or more, all adjustments being made through the capillary, which should be of from 1.5 to 2 mm. bore, according to the capacity of the toluene reservoir.

All danger of the toluene creeping into the capillary is removed, since the tubes *c* and *f* terminate in the same liquid which is contained in them.

This trap is compact, not easily broken, and is comparatively simple to construct. In addition to this, it lies within the plane of the reservoir and contact tubes.

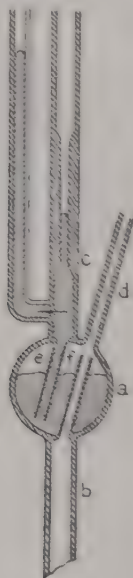


FIG. 3.

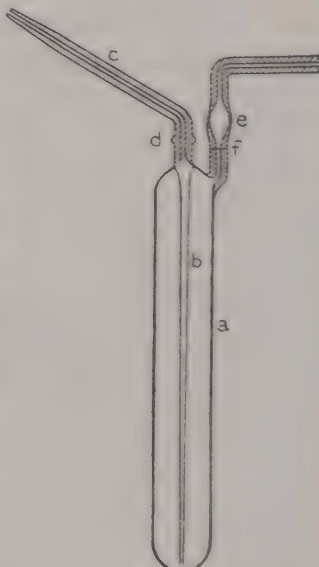


FIG. 4.

A NEW FORM OF PYKNOMETER FOR LIQUIDS.¹

The investigators, P. B. Davis and L. S. Pratt, have recently had occasion to carry out a large number of density determinations with various liquids. For this purpose a modified form of the Sprengel pyrometer, as described by Jones and Bingham² and Jones and Veazey,³ was first adopted, but was found to have the following disadvantages:

1. In instruments of large capacity (10 to 20 c.c.) the long capillary side-arm adds greatly to the weight and hence impairs the accuracy of the pyrometer.

¹Devised with L. S. Pratt. ²Amer. Chem. Journ., **34**, 48 (1905). ³Zeit. phys. Chem., **61**, 641 (1908).

2. The fragility of the older form makes rapid handling practically impossible.

3. The instrument is difficult to dry and polish before weighing.

To remove these defects the form shown in fig. 4 was devised, and has been found to be more convenient and accurate than the old form.

In the figure the symbols have the following significance:

(a) A reservoir of thin-walled glass tubing which may be of any desired capacity, those in use in this laboratory holding, respectively, about 6, 10, and 20 c.c.

(b) Tapering tube of thin glass reaching almost to the bottom of (a), and having a bore at the open end equal to or slightly greater than that of the capillary (0.5 to 0.75 mm.). This tube is of use in drying and filling the instrument.

(c) Outlet tube sealed on to the end of b. This is drawn out slightly at the end and is bent at an angle of 60° close to the reservoir.

(d) Slight enlargement in c which holds in position the wire used to suspend the pyknometer on the balance.

(e) Expansion bulb of sufficient size to accommodate the increased volume of any liquid when warmed 10° . If the instruments are used only at 25° this bulb need be only very small.

(f) Fine line etched around the capillary at the lower limit of the taper in the bulb e.

In adjusting the instrument when filled, a rubber tube is attached to the horizontal capillary above e, and the liquid blown out gently until the level in e just reaches the mark f. The excess of liquid is then removed from the end of c with filter paper. On removing the pressure, the level of the liquid in c falls until it comes to rest near the bend in the capillary, thereby lessening the danger from evaporation or accidental spilling after adjustment.

The advantages of this form of pyknometer can readily be seen, *e. g.*, the projecting arms are both short and hence not easily broken. Also, the net weight has been materially lessened, since the amount of necessary capillary has been reduced to a minimum. The instrument is also much easier to clean and dry before weighing than the older form.

This pyknometer may be provided with ground-on caps when used with alcohol or other volatile liquids, to prevent possible evaporation.

CHAPTER II.

THE CONDUCTIVITY AND VISCOSITY OF SOLUTIONS OF CERTAIN SALTS IN FORMAMID AS A SOLVENT.

BY P. B. DAVIS AND W. S. PUTNAM.

The work of Jones and his collaborators in the field of non-aqueous solvents and in mixtures of these solvents with one another, has thus far necessitated a comprehensive study of both the conductivity and viscosity of typical salts in methyl and ethyl alcohols, in acetone, and in glycerol—as well as in binary and ternary mixtures of these solvents with one another and with water. A complete review of all this work is to be found in Publication No. 210 of the Carnegie Institution of Washington, Chapter VII.

Because of the somewhat limited solubility of electrolytes in most organic solvents, the scope of this work has necessarily been somewhat limited in the case of the pure liquids themselves. This is especially true with acetone and the alcohols. Glycerol, however, notwithstanding its high viscosity, proved to be a remarkably good solvent.

Among the few remaining liquids suitable for such work, formamid, the one used in this investigation, is the most important. The fact that it has been studied so little in the past must be attributed to the difficulties encountered in obtaining a product pure enough for conductivity purposes.

Formamid, the first member of the series of acid amids of which acetamid is the best known representative, was first prepared by A. W. von Hoffman¹ in 1863, by heating anhydrous ethyl formate with dry ammonia in a sealed tube for some time, and then distilling the resulting product in a partial vacuum. A number of other methods of preparation have been devised, among the earlier ones being that of Behrend,² who heated a dry mixture of ammonium formate and urea to 140° and purified the oily residue by fractional distillation *in vacuo*. More recently Phelps and Deming³ improved Hoffman's method by carrying out the decomposition of the ethyl formate at a temperature below that at which ammonium formate is formed, thereby obtaining nearly the theoretical yield. In addition to the above, probably the most common method of preparing formamid is that depending on the dissociation of anhydrous ammonium formate by heat in an atmosphere of dry ammonia, as described for the first time also by Hoffman.⁴ By this method, with the latest improvements due to Freer and Sherman,⁵ pure formic acid is neutralized with dry ammonia and the resulting

¹Journ. Chem. Soc., **16**, 72 (1863). ²Lieb. Ann., **128**, 335 (1863). ³Centralblatt II, 1604 (1907).

⁴Ber. d. deutsch. chem. Gesell., **15**, 980 (1882). ⁵Amer. Chem. Journ., **20**, 223 (1898).

formate heated for several hours to 180° in an atmosphere of ammonia. In distilling the resulting brownish liquid under diminished pressure, a yield of 80 per cent of the theoretical was obtained. At lower pressures (0.5 to 2 mm.) a better yield resulted, since in this way the thermal decomposition was reduced to a minimum.

PREVIOUS WORK IN FORMAMID.

Until quite recently no investigation of the physical-chemical properties of this remarkable liquid had been made. A brief sketch of the recent work is given below.

In his preliminary paper on organic solvents, Walden mentions the marked similarity of formamid to water as compared with other liquids in its solvent action on inorganic salts, and in later papers he records some of its physical constants in comparison with other amids and with water, viz, the dielectric constant and association factors,¹ specific conductivity and molecular conductivity of the normal electrolyte $N(C_2H_5)_4I$,² and the viscosity.³ All of these constants were obtained with a product which, as will be shown later, was far from pure, although it may be pointed out that the first two constants are not appreciably affected by small changes in the purity of the solvent.

Turner and Merry,⁴ in their work on the molecular composition of trivalent nitrogen compounds, pointed out that the high association factor of formamid is one of its most striking characteristics, and they observed its similarity to water. They noted also that the association of formamid diminishes more rapidly with rise in temperature than that of water, and suggested that the solvent power for salts was largely due to its high molecular complexity.

Somewhat later, Walden,⁵ in a study of the temperature coefficient K , for organic liquids in the Ramsay and Shields equation for molecular surface-tension, found that in the case of formamid the value was far below that for non-associated liquids (2.12), having only the value 0.594 to 0.710; from these data he obtained an association factor in close agreement with that as determined by Turner and Merry.⁴

Dunstan and Kassel,⁶ while determining the fluidity of various binary mixtures, measured the viscosity of mixtures of formamid and *i*-amyl alcohol at both low and somewhat elevated temperatures, and noted a pronounced minimum in the fluidity curves at about 60 to 70 per cent of formamid at both temperatures, and also a slight maximum at about 10 to 20 per cent formamid for the lower temperature.

Rohler⁷ studied the solvent properties of formamid for organic salts and also the electrolysis of its solutions. He compared the density with that of water above the freezing-point and found no minimum,

¹Zeit. phys. Chem., **46**, 145, 175 (1906). ²*Ibid.*, **54**, 179 (1905). ³*Ibid.*, **55**, 230 (1906).

⁴Journ. Chem. Soc., **97**, 2076 (1910).

⁵Zeit. phys. Chem., **75**, 555 (1910). ⁶*Ibid.*, **76**, 367 (1911). ⁷Zeit. Elektrochem., **16**, 420 (1910).

as in the case of the latter, but that the solvent expanded linearly with rise in temperature, the variation of the specific volume being represented by $V = 0.8674 \times (10.000742t)$.

Rohler also found that, according to Faraday's law, copper dissolves in formamid at all dilutions, half as univalent and half as bivalent ions, at the anode. He obtained a good separation of copper with a weak current, but with a stronger current the metal separated as a dark slime. Similar results were obtained with lead, zinc, and tin. With all of these metals in air, more metal dissolved at the anode than separated at the cathode. The electrolysis of nickel, cobalt, iron, aluminium, and magnesium salts yielded no appreciable amount of metal at the cathode. Rohler also noted the formation of metallic formamidates and of crystalline double compounds, which will be considered in discussing the properties of formamid as compared with those of water.

In a quite recent paper Walden¹ gives an account of his cryoscopic work in this solvent. In his preliminary discussion he states, as his reason for adopting the freezing-point rather than the conductivity method for measuring dissociations, that the high specific conductivity of the solvent (as measured by him) rendered it impossible to obtain accurate data by the latter method. However, as will be pointed out later, by our method of preparing formamid a solvent may be obtained with a specific conductivity comparable with that of water, the loss of material being only one-third that experienced by Walden.

Walden determined the freezing-point constant of formamid, and gives the value 35.0 as the mean of six determinations, using urea, acetic ester, diethylsulphite, ethyl acetate, mesityloxide, and nitrana-line, respectively, as the solute. He also studied the dissociation of a number of electrolytes, including salts and both strong and weak acids, and pointed out that all binary salts are strongly ionized at relatively high concentrations, the ionization increasing slowly to the limit $\alpha = 100$, as in water; the limit, however, being reached at a smaller dilution in formamid. The same was found to hold for acids, except in the case of those where combination took place between solvent and solute, as in the case of some of the strong acids, the values found being smaller than those for water.

FORMAMID AS A SOLVENT.

Formamid is a clear, colorless, and somewhat viscous liquid, melting at 18°, and boiling under atmospheric pressure with partial decomposition at 200° to 212°. It reacts neutral to litmus and is quite hygroscopic, undergoing a slow hydrolysis at ordinary temperatures into ammonium formate. This solvent is the most closely allied to water in its properties of all the organic solvents. The two are miscible in

¹Bull. Imp. Acad. Sci., St. Petersburg (1911).

all proportions, neither being soluble to any extent in absolute ether, chloroform, benzol, hexane, etc.; nor do they dissolve appreciably the aromatic hydrocarbons, nitrobenzol, fats, oils, etc. Further similarity may be traced in their solvent action on metallic salts; thus, in the cold, cobalt and nickel salts yielding solutions in formamid similarly colored with those in water, although in some instances the formamid solutions undergo change in color on warming, which is probably due to a predominance of the unionized salt, since formamid undergoes a much sharper decrease in association with rise in temperature than water.

As Walden has pointed out, the similarity between water and formamid is still closer. Phosphorus and sulphur are practically equally insoluble in both, while iodine gives a brownish-yellow solution. Starch is also soluble in formamid, with formation in concentrated solution of a jelly, and on addition of formamid solution of iodine the starch solution turns intensely blue. The color, however, is less permanent than in water, owing to the slow action of the iodine on the solvent. The fluorescent dyes also exhibit like phenomena in formamid and in water, this being particularly marked in the case of eosin.

TABLE 5.

Physical constants.	Water.	Formamid.
Molecular weight	18	45
Melting-point	0°	1.5–2.1 (Walden).
Boiling-point 760 mm	100°	200–212
Density 0°/4°	.9999	1.151 (Walden, Davis).
Dielectric constant	81 (Drude) ²⁵⁰	84 (Walden).
Association factor 30°	3.81 (Ramsay-Shields).	6.18 (Turner and Merry).
K-surface tension 20° to 30°		0.65 (Turner and Merry).
Minimum specific conductivity	4×10^{-8} .	2.8×10^{-6} (Davis and Putnam).
Average specific conductivity working values.	1.5×10^{-6} .	2.7×10^{-5} (Davis and Putnam).
Viscosity, 25°	0.00891 (Thorpe and Rodger).	0.0324 (Davis).
Dissociation of $N(C_2H_5)_4I$ at $V = 100$.	91 p. ct.	93 p. ct. (Walden); 98 p. ct. (Davis and Putnam).

Bruni and Mannuelli¹ further show that just as water hydrolyzes the salts of weak bases, such as those of bismuth and antimony, forming unstable basic salts; formamid by a process of aminolysis may form basic salts of these same metals; and Rohler,² in extending this work has isolated characteristic basic salts of copper, cobalt, nickel, and zinc. He has also obtained amidates similar to hydrates, of which $PbCl_2 \cdot HCONH_2$ is an example, as well as metal formamidates having the general composition $Me(HNCOH)_2 \cdot 2HCONH_2$, where Me may be either copper, nickel, cobalt, or zinc.

In addition to the above, Rohler has noticed the formation of well-defined crystalline compounds of formamid with the halogen acids, corresponding to the well-known mono-, di-, and tri-hydrates.

¹Zeit. Elektrochem, **11**, 554 (1905).²Ibid., **16**, 418 (1910).

As is now well established, the dielectric constant of the solvent is a measure of its own association, and therefore a measure of its dissociating power for electrolytes. Of the common solvents, water has the highest dielectric constant, and is the best dissociant. Formamid, however, has a higher dielectric constant than water, as will be shown by referring to the table of physical constants of the two solvents (table 5), and should therefore be a better dissociant, which in our discussion will be pointed out to be the fact.

PURIFICATION OF THE SOLVENT.

It might be well to state at the outset, that neither a clean melting-point nor a constant boiling-point is a sufficient criterion for conductivity purposes as to the purity of the solvent, since it has been found by ourselves and others, that a constant-boiling liquid such as formamid, may be separated into fractions of widely different specific conductivities. That this is true is due, no doubt, in this particular case, to the fact that minute quantities of the products of hydrolysis, such as would have no measurable effect on the apparent boiling-point of the liquid, on account of the high dissociating power of the formamid, produce a marked increase in its conductivity.

The chief criterion, therefore, in judging of the purity of the solvent used in this investigation was its specific conductivity. The material with which we started was obtained from Kahlbaum, and had a specific conductivity of about 674×10^{-5} , or about that of tap-water. Samples obtained from Bender and Hobein, from Schuchardt, and from Hoffman and Kropf proved from the conductivity standpoint to be little or no better than the above.

As has already been mentioned, formamid is hygroscopic, forms a true solution with water, and subsequently undergoes slow hydrolysis into ammonium formate. The first problem, therefore, that must be solved, was the removal of any dissolved water not already acted on; second, the removal of the products of hydrolysis already present. The method of fractional distillation made it necessary to design and construct suitable apparatus for distillation in comparatively high vacuo.

A third problem presented itself in connection with the preservation and subsequent manipulation of the solvent and of solutions in it, in such a manner as to incur minimum exposure to moisture. In addition, the expense of the solvent made necessary the recovery of it from solutions of salts in this solvent, with the least possible loss by decomposition.

The removal of dissolved water was finally effected by the use of carefully dehydrated sodium sulphate. After testing a number of other dehydrating agents, such as magnesium sulphate, calcium chloride, sulphuric acid *in vacuo*, etc., it was found that sodium sulphate

produced a smaller loss of materials from combination with it than any of the other dehydrating agents studied.

Formamid was therefore allowed to stand for several weeks over anhydrous sodium sulphate, in carefully sealed, glass-stoppered bottles, and placed in a cool, dark room. An attempt was made to effect a preliminary purification of formamid by fractional crystallization; but the end-product, after several fractionations, invariably showed a higher conductivity than the original substance. We were therefore forced to conclude, as were Freer and Sherman in preparing formamid to study its sodium salts, that a properly conducted distillation was the best process available.

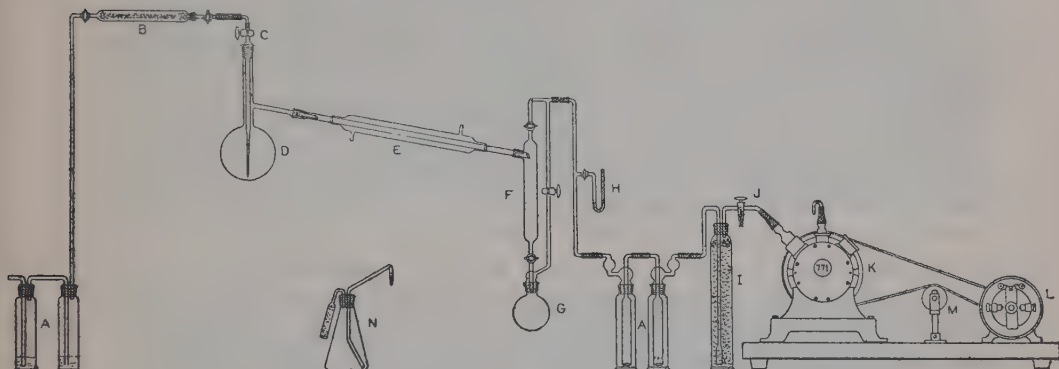


FIG. 5.

The apparatus finally adopted for distillation is shown diagrammatically in figure 5. By placing the various parts in parallel rows it was possible to mount the whole apparatus upon a desk-space of only $2\frac{1}{2}$ feet square, as is shown in the photograph (plate 1). This condensed arrangement of the apparatus given in figure 5 is photographed in two views in plate 1, and is the perfected apparatus with the exception of the distillation head and the position of the manometer.

In this apparatus, with all the stopcocks closed, a vacuum of 0.5 mm. was easily maintained by the Gaede pump (fig. 5, K). This pump was mounted, together with a $\frac{1}{12}$ -horsepower motor (fig. 5, L), controlling rheostat not shown, idler (fig. 5, M), and switch, on a heavy maple wood base, provided with carrying handles and rubber feet.

During the actual process of distillation the vacuum rose to from 1.5 to 2.5 mm., since, on account of the high viscosity of the liquid, it was necessary to keep a fairly rapid current of air flowing in through the stopcock and drawn-out portion of the distillation head (fig. 5, E), in order to keep the liquid agitated and prevent the violent bumping which usually attended distillation in a high vacuum. The drying of this current of air sufficiently, and the proper method of introducing it, proved to be among the most serious difficulties encountered. The method finally adopted is shown in figure 5. The air, before entering

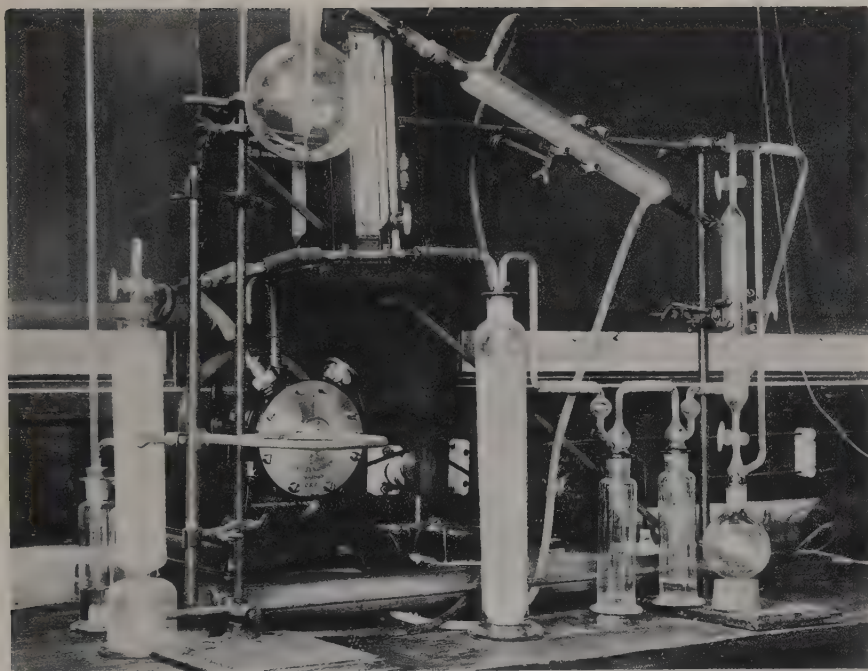
the distillation flask, passed through a soda-lime tower (not shown in the drawing, but appears on the left in plate 1; then through the two wash bottles (fig. 5, A), and finally over phosphorus pentoxide contained in the long tube B, which was protected by two glass stopcocks, the one sealed permanently into the tube and the other securely fastened with sealing-wax in the left-hand tapered end of B. This joint made it possible to open B in renewing the phosphorus pentoxide. From B, the current of air passed into C, through a short rubber connection and a right-angle glass bend, the open end of which is connected with C by a rubber joint made air-tight with rubber cement.

The distillation head C consisted of a short projecting tube, a well-ground stopcock of large bore; the ground connection with the 750 c.c. distilling flask D, and the long inner tube reaching to the bottom of the flask and drawn to a capillary at the end, so as to cause the air to bubble in a fine stream through the liquid. Connection between the flask and the condenser was effected by a ground joint designed to prevent the liquid distilling over from coming in contact with the stopcock grease used in making the joint air-tight. The condenser was also ground into the Axtell receiver F, which is too well known to require further description, other than to state that the capacity of the barrel was about 100 c.c. and that of the small bulb 250 c.c. The receiver allowed the removal of different fractions without interrupting the vacuum.

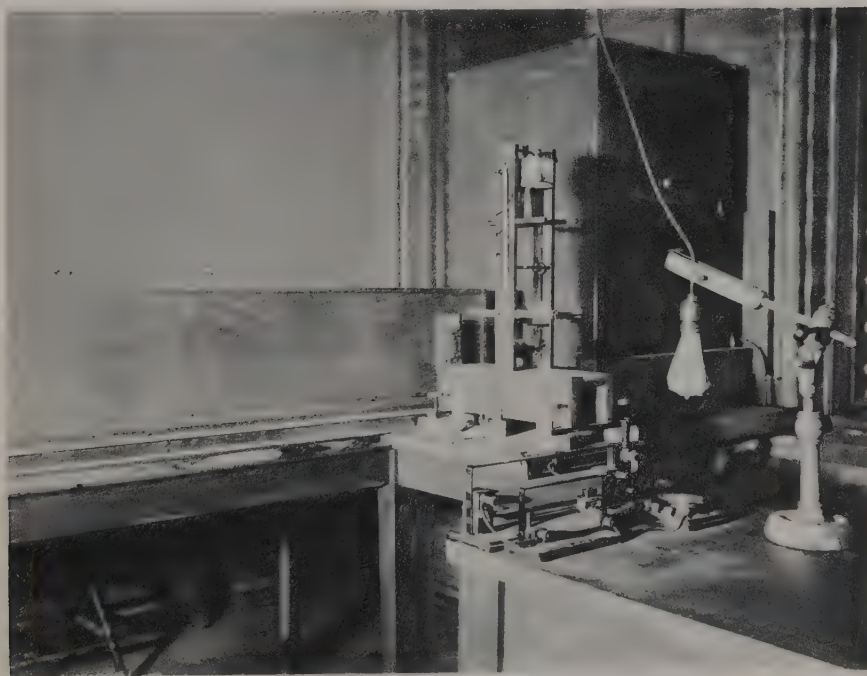
The receiver was connected with the pump K, through the gas wash bottles A', the soda-lime tower I, and the three-way stopcock J. One of the wash bottles was filled just to the upper level of the holes in the inner cylinder with sulphuric acid; the other was empty, serving as a trap in the case of back-pressure. The construction of the wash bottles secured a maximum exposure of acid to the possible alkaline vapors (NH_3) without appreciable back-pressure.

Liquid formamid was introduced into the flask at any time during the distillation without destroying the vacuum, by closing the stopcock on C, temporarily disconnecting the air inlet, and attaching at the same point the flask and siphon N. On opening the stopcock the diminished pressure in the flask drew in any liquid in N.

During the distillation the flask was immersed in a bath of hardened cottonseed oil ("Crisco"), into which the thermometer dipped. Ordinary rectified cottonseed oil was first used, but this was soon discontinued, since the oil quickly became rancid and offensive when heated. The "Crisco," however, remains sweet and untainted even after continued use. The temperature in the outer bath was maintained at from 10° to 15° higher than the boiling-point of the liquid at a given pressure, the usual temperature being 100° to 115° . In the apparatus used in the preliminary work a thermometer was sealed into the air-inlet tube of C, with its bulb well down in the flask, and the boiling-point of the



1. Distilling Apparatus.



2. Spectroscope with Cover.

liquid was observed; but this thermometer was subsequently discarded and the temperature controlled solely by the thermometer in the outer bath, so as to obtain about 100 c.c. of distillate every 15 minutes.

As a rule, starting with Kahlbaum's so-called c. p. formamid, from three to four distillations yielded a product sufficiently pure for our purpose. The decrease in the conductivity with successive distillation is shown in table 6:

TABLE 6.—*Specific Conductivity.*[Original material, 674.0×10^{-4} .]

	First distillation.	Second distillation.	Third distillation.
First fraction	785.8×10^{-5}	204.2×10^{-5}	24.6×10^{-5}
Second fraction	435.0×10^{-5}	153.8×10^{-5}	10.3×10^{-5}
Third fraction	112.3×10^{-5}	67.4×10^{-5}	4.8×10^{-5}

While the end-fraction in this case was sufficiently pure for use, a fourth distillation yielded a product with a conductivity of about $3-4 \times 10^{-5}$. Although the exact minimum conductivity of this solvent has thus far not been ascertained, we have obtained small lots with a specific conductivity of 2.8×10^{-6} to 4.7×10^{-6} , or from 2 to 3 times the value for the conductivity water used in this laboratory. Walden used in his work a product with a conductivity of 7.5×10^{-4} , but obtained a small fraction of about 10 per cent of the original material, with a conductivity of 4.7×10^{-5} . Our solvent was from 35 to 40 per cent of the original volume with a maximum specific conductivity of 4.8×10^{-5} , with a minimum of 1.37×10^{-5} and an average of 2.7×10^{-5} .

SALTS.

On account of the instability of the solvent formamid in the presence of moisture, the salts used in this investigation were all dehydrated with special care at the highest temperature which it was possible to use for these substances.

SOLUTIONS.

The more concentrated solutions in formamid were made up by direct weighing; the more dilute by diluting the more concentrated. This operation was much facilitated by the use of two burettes holding 50 and 10 cm. respectively; the one being employed for the solvent, the other for the one-tenth normal solution. Each burette was connected with the reservoir containing the solvent or the solution, by a siphon provided with a glass stopcock, access of moisture being prevented by calcium chloride tubes connected with both the burettes and the reservoirs.

The solvent was kept in half-liter glass-stoppered Erlenmeyer flasks, and the solutions when made up were preserved in 35 c.c. flasks of similar design, which were sealed with rubber cement.

On account of the high price of the solvent, only 25 c.c. of each solution was prepared, this amount serving both for conductivity and viscosity measurements. All operations in preparing the solutions were carried out at 20°.

APPARATUS.

Conductivity apparatus.—The conductivity apparatus was identical with that employed in our earlier work on binary and ternary mixtures of water, acetone, and glycerol; the method of obtaining duplicate readings and other details being exactly the same as in the earlier work, excepting the use of a rocking commutator with mercury contacts instead of the two-blade, double-throw switch used in reading both ends of the bridge, the object being to eliminate as nearly as possible all external resistance. The conductivity cells were of the type recently employed in this laboratory for work with non-aqueous solvents, and were carefully calibrated at regular intervals.

Viscosity apparatus.—This was essentially the same as in our earlier investigations. We have designed and used an improved support for the viscosimeters, which is particularly well adapted to our new thermostat. A new pyknometer has also been devised, which has proved to have advantages over the older form. (See Chapter I.)

Thermostats.—The new form of constant-temperature bath for conductivity and viscosity investigations has already been fully described in Chapter VI of Publication No. 210 of the Carnegie Institution of Washington.

DISCUSSION OF RESULTS.

Tables 8 to 27, inclusive, give the molecular conductivity, dissociation, viscosity, and fluidity, as well as the temperature coefficients both of conductivity and fluidity, for all of the salts studied. Measurements were made at 15°, 25°, and 35°.

TABLE 7.—Comparison of the Various Solvents.

Solvent.	Dielectric constant.	Association factor.	Viscosity at 25°.
HCN.....	95		
HCONH ₂	94	6.18	0.0326
H ₂ O.....	81.7	3.81	0.0089
CH ₃ OH.....	32.5	3.43	0.0056
C ₂ H ₅ OH.....	21.7	2.74	0.0111
C ₃ H ₅ (OH) ₃	16.5	1.80	5.854
CH ₃ —CO—CH ₃	20.7	1.26	0.0035

TABLE 8.—*Sodium Bromide in Formamid.*[K,¹ for 15° = 1.53×10^{-5} ; for 25° = 1.99×10^{-5} ; for 35° = 2.46×10^{-5}].

V	Molecular conductivity.			Dissociation.			Temperature coefficients.			
							Per cent.		Conductivity units.	
	15°	25°	35°	15°	25°	35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
2	11.83	15.53	19.76	62.1	63.1	63.4	0.0313	0.0272	0.370	0.423
4	13.80	18.01	22.82	72.4	73.2	73.6	0.0305	0.0267	0.421	0.481
10	16.20	21.09	26.64	85.0	85.7	86.0	0.0302	0.0263	0.489	0.555
50	17.46	22.62	28.55	91.6	91.9	92.1	0.0296	0.0262	0.516	0.593
200	18.79	24.36	30.59	98.6	98.9	98.7	0.0296	0.0256	0.557	0.623
400	19.06	24.62	30.99	100.0	100.0	100.0	0.0292	0.0259	0.0556	0.637

V	Viscosity and fluidity.						Temperature coefficients of fluidity.	
	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°	15 to 25°	25 to 35°
2	0.05578	0.04081	0.03120	17.93	24.50	32.05	0.0367	0.0308
4	0.04883	0.03678	0.02837	20.48	27.19	35.25	0.0328	0.0296
10	0.04523	0.03413	0.02666	22.11	29.30	37.51	0.0325	0.0280
Solv.	0.04274	0.03194	0.02511	23.40	31.31	39.83	0.0338	0.0272

¹K is the specific conductivity of the solvent.TABLE 9.—*Sodium Iodide in Formamid.*[K, for 15° = 2.23×10^{-5} ; for 25° = 2.83×10^{-5} ; for 35° = 3.48×10^{-5}].

V	Molecular conductivity.			Dissociation.			Per cent.		Conductivity units.	
	15°	25°	35°	15°	25°	35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
2	11.92	15.71	20.01	64.7	65.6	66.1	0.0318	0.0274	0.379	0.430
4	14.17	18.57	23.59	76.9	77.5	78.0	0.0311	0.0270	0.440	0.502
10	15.91	20.67	26.05	86.3	86.3	86.1	0.0299	0.0260	0.476	0.538
50	17.17	22.33	28.17	93.2	93.2	93.1	0.0301	0.0262	0.516	0.584
200	18.27	23.80	29.98	99.1	99.3	99.1	0.0303	0.0260	0.553	0.618
400	18.43	23.96	30.25	100.0	100.0	100.0	0.0300	0.0263	0.553	0.629

V	Viscosity and fluidity.						Temperature coefficients of fluidity.	
	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°	15 to 25°	25 to 35°
2	0.05425	0.03997	0.03065	18.43	25.02	32.63	0.0357	0.0304
4	0.04822	0.03640	0.02800	20.74	27.47	35.71	0.0325	0.0300
10	0.04532	0.03381	0.02653	22.07	29.58	37.69	0.0340	0.0274
Solv.	0.04307	0.03302	0.02570	23.22	30.29	38.91	0.0304	0.0285

TABLE 10.—*Sodium Chromate in Formamid.*[K, for 15° = 1.30×10^{-5} ; for 25° = 1.65×10^{-5} ; for 35° = 2.03×10^{-5} .]

V	Molecular conductivity.			Dissociation.			Per cent.		Conductivity units.	
	15°	25°	35°	15°	25°	35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
10	24.57	33.66	42.66				0.0316	0.0267	0.809	0.900
50	31.46	41.48	52.18				0.0319	0.0258	1.002	1.070
200	34.34	44.82	56.38				0.0305	0.0258	1.048	1.156
400	39.00	50.79					0.0302		1.179	
800	42.64	55.07	69.16				0.0292	0.0256	1.243	1.409
1,600	72.06	93.51	116.44				0.0298	0.0245	2.145	2.293

V	Viscosity and fluidity.						Temperature coefficients of fluidity.	
	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°	15 to 25°	25 to 35°
10	0.04966	0.03633		20.14	27.30			
Solv.	0.04301	0.03221		23.25	31.05			

TABLE 11.—*Potassium Chloride in Formamid.*[K, for 15° = 2.94×10^{-6} ; for 25° = 3.75×10^{-6} ; for 35° = 4.69×10^{-6} .]

V	Molecular conductivity.			Dissociation.			Per cent.		Conductivity units.	
	15°	25°	35°	15°	25°	35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
2	14.12	18.25	22.94	67.9	68.3	68.7	0.0292	0.0257	0.413	0.469
4	16.15	20.84	26.13	77.6	78.0	78.3	0.0290	0.0252	0.469	0.529
10	18.06	23.27	28.99	86.8	87.1	86.8	0.0288	0.0246	0.521	0.572
50	19.27	24.94	31.12	92.6	93.3	93.2	0.0294	0.0248	0.567	0.618
200	20.66	26.60	33.10	99.3	99.5	99.1	0.0288	0.0244	0.594	0.650
400	20.80	26.73	33.39	100.0	100.0	100.0	0.0285	0.0249	0.593	0.666

V	Viscosity and fluidity.						Temperature coefficients of fluidity.	
	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°	15 to 25°	25 to 35°
2	0.05251	0.03922	0.03000	19.04	25.50	33.33	0.0339	0.0307
4	0.04724	0.03572	0.02794	21.17	28.00	35.79	0.0323	0.0278
10	0.04457	0.03386	0.02642	21.94	29.53	37.85	0.0338	0.0282
Solv.	0.04304	0.03256	0.02542	23.23	30.71	39.34	0.0322	0.0281

TABLE 12.—*Potassium Iodide in Formamid.*[K, for 15°=2.23×10⁻⁵; for 25°=2.83×10⁻⁵; for 35°=3.48×10⁻⁵.]

V	Molecular conductivity.			Dissociation.			Per cent.		Conductivity units.	
	15°	25°	35°	15°	25°	35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
2	14.42	18.67	23.29	70.7	71.0	71.0	0.0295	0.0247	0.425	0.462
4	16.32	21.05	26.34	80.0	80.1	80.3	0.0290	0.0251	0.473	0.529
10	18.23	23.45	29.21	89.4	89.2	89.0	0.0286	0.0246	0.522	0.576
50	19.25	24.87	31.03	94.4	94.6	94.5	0.0292	0.0248	0.562	0.616
200	20.39	26.28	32.81	100.0	100.0	100.0	0.0289	0.0248	0.589	0.653
400	20.26	26.29	32.82							

V	Viscosity and fluidity.						Temperature coefficients of fluidity.	
	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°	15 to 25°	25 to 35°
2	0.04982	0.03710	0.02884	20.07		34.67	0.0343	0.0286
4	0.04631	0.03525	0.02716	21.59	28.37	36.81	0.0314	0.0298
10	0.04418	0.03353	0.02629	22.64	29.82	38.04	0.0318	0.0274
Solv.	0.04307	0.03302	0.02570	23.22	30.29	38.91	0.0304	0.072

TABLE 13.—*Potassium Sulphocyanate in Formamid.*[K, for 15°=1.07×10⁻⁵; for 25°=1.37×10⁻⁵; for 35°=1.69×10⁻⁵.]

V	Molecular conductivity.			Dissociation.			Per cent.		Conductivity units.	
	15°	25°	35°	15°	25°	35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
2	15.15	19.10	24.28	70.0	69.2	70.4	0.0261	0.0271	0.395	0.518
4	17.42	22.31	27.87	80.6	80.8	80.8	0.0281	0.0249	0.489	0.556
10	19.04	24.38	30.35	88.0	88.3	88.0	0.0280	0.0245	0.534	0.597
50	20.02	25.61	32.16	92.6	92.8	93.3	0.0279	0.0256	0.558	0.655
200	21.21	27.19	33.89	98.1	98.5	98.3	0.0282	0.0246	0.598	0.670
400	21.62	27.60	34.47	100.0	100.0	100.0	0.0277	0.0249	0.598	0.687

V	Viscosity and fluidity.						Temperature coefficients of fluidity.	
	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°	15 to 25°	25 to 35°
2	0.04891	0.03657	0.02838	20.45	27.35	35.24	0.0337	0.0287
4	0.04585	0.03473	0.02713	21.81	28.79	36.86	0.0320	0.0280
10	0.04369	0.03280	0.02574	22.89	30.49	38.85	0.0332	0.0274
Solv.	0.04294	0.03258	0.02554	23.29	30.69	39.15	0.0314	0.0276

TABLE 14.—*Ammonium Bromide in Formamid.*[K, for 15° = 2.94×10^{-5} ; for 25° = 3.76×10^{-5} ; for 35° = 4.67×10^{-5} .]

V	Molecular conductivity.			Dissociation.			Per cent.		Conductivity units.	
	15°	25°	35°	15°	25°	35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
2	16.31	20.85	25.79	70.6	70.6	70.0	0.0278	0.0237	0.454	0.494
4	18.21	23.31	28.88	78.8	78.9	78.3	0.0280	0.0247	0.510	0.557
10	20.57	26.21	32.53	89.0	88.7	88.3	0.0274	0.0241	0.564	0.632
50	21.82	27.94	34.82	94.4	94.6	94.5	0.0280	0.0246	0.612	0.688
200	22.63	28.83	35.93	97.9	97.6	97.5	0.0274	0.0246	0.620	0.710
400	23.11	29.54	36.86	100.0	100.0	100.0	0.0278	0.0248	0.643	0.732

V	Viscosity and fluidity.						Temperature coefficients of fluidity.	
	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°	15 to 25°	25 to 35°
2	0.04795	0.03607	0.02776	20.86	27.73	36.02	0.0330	0.0299
4	0.04550	0.03455	0.02680	21.98	28.94	37.31	0.0317	0.0289
10	0.04399	0.03273	0.02635	22.73	30.55	37.95		
Solv.	0.04304	0.03256	0.02542	23.23	30.71	39.34	0.0322	0.0281

TABLE 15.—*Ammonium Iodide in Formamid.*[K, for 15° = 3.68×10^{-5} ; for 25° = 4.71×10^{-5} ; for 35° = 5.87×10^{-5} .]

V	Molecular conductivity.			Dissociation.			Per cent.		Conductivity units.	
	15°	25°	35°	15°	25°	35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
2	16.90	21.70	26.80	73.6	73.1	72.5	0.0284	0.0281	0.480	0.610
4	18.78	24.06	29.88	81.8	81.0	80.8	0.0281	0.0240	0.528	0.582
10	20.48	26.32	32.44	89.2	88.6	87.7	0.0285	0.0233	0.584	0.612
50	21.31	27.39	33.92	92.8	92.3	91.2	0.0285	0.0238	0.608	0.653
100	22.20	28.40	35.40	96.7	95.7	95.8	0.0279	0.0246	0.620	0.700
400	22.96	29.69	36.97	100.0	100.0	100.0	0.0293	0.0245	0.673	0.728

V	Viscosity and fluidity.						Temperature coefficients of fluidity.	
	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°	15 to 25°	25 to 35°
2	0.05091	0.03856	0.03007	19.64	25.93	33.26	0.0320	0.0282
4	0.04571	0.03417	0.02669	21.88	29.27	37.47	0.0292	0.0280
10	0.04367	0.03311	0.02607	22.90	30.20	38.36	0.0319	0.0270
Solv.	0.04201	0.03207	0.02496	23.80	31.18	40.06	0.0310	0.0285

TABLE 16.—*Tetramethylammonium Chloride in Formamid.*[K, for 15° = 1.53×10^{-5} ; for 25° = 1.99×10^{-5} ; for 35° = 2.46×10^{-5}]

V	Molecular conductivity.			Dissociation.			Per cent.		Conductivity units.	
	15°	25°	35°	15°	25°	35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
2	14.62	18.72	23.38	68.6	68.5	68.1	0.0280	0.0249	0.410	0.466
4	16.92	21.80	27.27	79.4	79.7	79.4	0.0288	0.0251	0.488	0.547
10	18.37	23.65	29.32	86.2	86.5	85.4	0.0287	0.0240	0.528	0.567
50	19.64	25.32	31.65	92.1	92.6	92.1	0.0289	0.0250	0.568	0.633
200	21.19	27.34	34.11	99.5	100.0	99.3	0.0290	0.0248	0.615	0.677
400	21.30	27.34	34.35	100.0	100.0	100.0	0.0283	0.0256	0.604	0.701

V	Viscosity and fluidity.						Temperature coefficients of fluidity.	
	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°	15 to 25°	25 to 35°
2	0.04775	0.03578	0.02791	20.94	27.95	35.83	0.0335	0.0282
4	0.04503	0.03427	0.02679	22.21	29.18	37.33	0.0314	0.0279
10	0.04394	0.03313	0.02601	22.76	30.18	38.45	0.0326	0.0274
Solv.	0.04274	0.03194	0.02511	23.40	31.31	39.83	0.0338	0.0272

TABLE 17.—*Tetraethylammonium Iodide in Formamid.*[K, for 15° = 2.47×10^{-5} ; for 25° = 3.17×10^{-5} ; for 35° = 3.94×10^{-5}]

V	Molecular conductivity.			Dissociation.			Per cent.		Conductivity units.	
	15°	25°	35°	15°	25°	35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
2	11.78	15.42	19.47	62.6	63.5	64.0	0.0309	0.0262	0.364	0.405
4	13.86	18.10	22.78	73.7	74.5	74.9	0.0306	0.0259	0.424	0.468
10	15.74	20.31	25.31	83.7	83.6	83.2	0.0290	0.0246	0.457	0.500
50	17.60	22.69	28.47	93.6	93.5	93.6	0.0298	0.0255	0.509	0.578
100	18.45	23.79	29.85	98.1	98.0	98.1	0.0289	0.0255	0.534	0.606
200	18.81	24.28	30.43	100.0	100.0	100.0	0.0291	0.0253	0.547	0.615

V	Viscosity and fluidity.						Temperature coefficients of fluidity.	
	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°	15 to 25°	25 to 35°
2	0.04879	0.03618	0.02802	20.50	27.64	35.68	0.0349	0.0291
4	0.04573	0.03486	0.02687	21.87	28.69	37.22	0.0312	0.0297
10	0.04431	0.03336	0.02607	22.57	29.98	38.36	0.0328	0.0280
Solv.	0.04284	0.03256	0.02561	23.34	30.71	39.05	0.0316	0.0271

TABLE 18.—*Rubidium Chloride in Formamid.*[K, for 15° = 2.47×10^{-5} ; for 25° = 3.17×10^{-5} ; for 35° = 3.94×10^{-5} .]

V	Molecular conductivity.			Dissociation. °			Per cent.		Conductivity units.	
	15°	25°	35°	15°	25°	35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
2	14.28	18.46	23.10	67.7	68.1	68.6	0.0292	0.0251	0.418	0.464
4	16.31	21.00	26.17	77.3	77.5	78.0	0.0288	0.0251	0.469	0.527
10	18.77	24.09	30.10	89.0	88.9	89.3	0.0283	0.0249	0.532	0.601
50	19.84	25.54	31.82	94.1	94.3	94.4	0.0287	0.0246	0.570	0.628
100	20.59	26.49	33.03	97.6	97.8	98.0	0.0287	0.0247	0.590	0.654
200	21.09	27.08	33.69	100.0	100.0	100.0	0.0284	0.0244	0.599	0.661
V	Viscosity and fluidity.						Temperature coefficients of fluidity.			
	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°	15 to 25°	25 to 35°		
2	0.05246	0.03869	0.02961	19.06	25.85	33.77	0.0356	0.0308		
4	0.04773	0.03606	0.02778	20.95	27.73	36.00	0.0324	0.0298		
10	0.04486	0.03396	0.02623	22.29	29.45	38.12	0.0321	0.0295		
Solv.	0.04284	0.03256	0.02561	23.34	30.71	39.05	0.0316	0.0271		

TABLE 19.—*Rubidium Bromide in Formamid.*[K, for 15° = 4.79×10^{-5} ; for 25° = 6.07×10^{-5} ; for 35° = 7.62×10^{-5} .]

V	Molecular conductivity.			Dissociation.			Per cent.		Conductivity units.	
	15°	25°	35°	15°	25°	35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
4	16.36	21.26	26.52	79.8	81.1	81.2	0.0300	0.0247	0.490	0.526
10	18.47	23.79	29.63	90.1	90.8	90.7	0.0286	0.0245	0.532	0.584
50	20.49	26.21	32.68	100.0	100.0	100.0	0.0279	0.0247	0.572	0.647
100	20.36	26.27	32.71							
V	Viscosity and fluidity.						Temperature coefficients of fluidity.			
	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°	15 to 25°	25 to 35°		
2	Solution supersaturated at 25°.									
4	0.04661	0.03501	0.02717	21.46	28.56	36.81	0.0331	0.0289		
10	0.04462	0.03394	0.02648	22.41	29.46	37.76	0.0315	0.0282		
Solv.	0.04312	0.03260	0.02564	23.19	30.68	39.00	0.0323	0.0271		

TABLE 20.—*Rubidium Iodide in Formamid.*[K, for 15° = 3.68×10^{-5} ; for 25° = 4.71×10^{-5} ; for 35° = 5.87×10^{-5} .]

V	Molecular conductivity.			Dissociation.			Per cent.		Conductivity units.	
	15°	25°	35°	15°	25°	35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
2	14.73	19.01	23.78	72.4	72.0	72.2	0.0290	0.0251	0.428	0.477
4	16.87	21.71	27.21	82.9	82.2	82.6	0.0287	0.0253	0.484	0.550
10	18.60	24.00	29.83	91.4	90.9	90.5	0.0290	0.0243	0.540	0.583
50	19.59	25.27	31.49	96.3	95.7	95.6	0.0290	0.0246	0.568	0.622
100	20.23	26.06	32.52	99.5	98.7	98.7	0.0288	0.0248	0.568	0.646
200	20.34	26.41	32.95	100.0	100.0	100.0	0.0298	0.0248	0.607	0.654

V	Viscosity and fluidity.						Temperature coefficients of fluidity.	
	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°	15 to 25°	25 to 35°
2	0.04945	0.03516	0.02865	20.22	27.66	34.90	0.0368	0.0265
4	0.04643	0.03503	0.02737	21.54	28.55	36.54	0.0325	0.0280
10	0.04432	0.03348	0.02634	22.56	29.87	37.97	0.0324	0.0271
Solv.	0.04201	0.03207	0.02496	23.80	31.18	40.06	0.0310	0.0285

TABLE 21.—*Rubidium Nitrate in Formamid.*[K, for 15° = 2.47×10^{-5} ; for 25° = 3.17×10^{-5} ; for 35° = 3.94×10^{-5} .]

V	Molecular conductivity.			Dissociation.			Per cent.		Conductivity units.	
	15°	25°	35°	15°	25°	35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
4	16.20	20.79	25.85	77.7	77.6	77.6	0.0283	0.0243	0.459	0.506
10	18.85	24.07	30.00	90.4	89.8	90.1	0.0277	0.0246	0.522	0.593
50	20.22	25.97	32.23	97.0	96.9	96.8	0.0284	0.0241	0.575	0.626
100	20.85	26.80	33.31	100.0	100.0	100.0	0.0285	0.0243	0.595	0.651
200	20.76	26.68	33.02							

V	Viscosity and fluidity.						Temperature coefficients of fluidity.	
	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°	15 to 25°	25 to 35°
4	0.04586	0.03430	0.02673	21.81	29.16	37.41	0.0337	0.0283
10	0.04417	0.03346	0.02622	22.64	29.89	38.15	0.0320	0.0276
Solv.	0.04284	0.03256	0.02561	23.34	30.71	39.05	0.0316	0.0271

TABLE 22.—*Cæsium Chloride in Formamid.*[K, for 15° = 1.34×10^{-5} ; for 25° = 1.72×10^{-5} ; for 35° = 2.10×10^{-5} .]

V	Molecular conductivity.			Dissociation.			Per cent.		Conductivity units.	
	15°	25°	35°	15°	25°	35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
4	16.83	21.69	27.15	78.6	78.8	78.7	0.0289	0.0252	0.486	0.546
10	18.75	24.09	30.03	87.6	87.5	87.1	0.0285	0.0247	0.534	0.594
200	21.40	27.54	34.49	100.0	100.0	100.0	0.0287	0.0252	0.614	0.695
400	21.06	27.15	34.11				0.0289	0.0256	0.609	0.696
V	Viscosity and fluidity.						Temperature coefficients of fluidity.			
	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°	15 to 25°	25 to 35°		
4	0.04735	0.03578	0.02789	21.12	27.95	35.86	0.0323	0.0283		
10	0.04481	0.03395	0.02654	22.32	29.46	37.68	0.0320	0.0279		
Solv.	0.04317	0.03245		23.16	30.81		0.0000			

TABLE 23.—*Cæsium Nitrate in Formamid.*[K, for 15° = 1.34×10^{-5} ; for 25° = 1.72×10^{-5} ; for 35° = 2.10×10^{-5} .]

V	Molecular conductivity.			Dissociation.			Per cent.		Conductivity units.	
	15°	25°	35°	15°	25°	35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
4	17.00	21.79	27.10	78.2	78.1	78.3	0.0282	0.0244	0.479	0.531
10	18.90	24.23	29.92	86.9	86.8	86.4	0.0282	0.0235	0.533	0.569
100	21.36	27.42	33.99	98.2	98.3	98.2	0.0284	0.0240	0.606	0.657
200	21.75	27.90	34.61	100.0	100.0	100.0	0.0283	0.0241	0.615	0.671
400	21.59	27.64	34.43				0.0280	0.0246	0.605	0.679
V	Viscosity and fluidity.						Temperature coefficients of fluidity.			
	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°	15 to 25°	25 to 35°		
4	0.04614	0.03478	0.02725	21.67	28.75	36.70	0.0327	0.0276		
10	0.04456	0.03362	0.02632	22.44	29.74	37.9	0.0325	0.0277		
Solv.	0.04317	0.03245		23.16	30.81					

TABLE 24.—*Lithium Nitrate in Formamid.*

V	Molecular conductivity.			Dissociation.			Per cent.		Conductivity units.	
	15°	25°	35°	15°	25°	35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
2	12.16	15.57		66.0	65.8		0.0280		0.341	
4	14.10	18.07		76.5	76.4		0.0281		0.397	
10	16.11	20.58	25.54	87.5	87.0	86.9	0.0277	0.0241	0.447	0.496
50	17.38	22.29	27.68	94.4	94.2	94.1	0.0283	0.0242	0.491	0.539
200	18.42	23.66	29.34	100.0	100.0	99.8	0.0284	0.0240	0.524	0.568
400	18.23	23.63	29.40			100.0	0.0296	0.0244	0.540	0.577

V	Viscosity and fluidity.						Temperature coefficients of fluidity.	
	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°	15 to 25°	25 to 35°
2	0.05191	0.03873	0.03019	19.26	25.82	33.12	0.0340	0.0283
4	0.04720	0.03571	0.02786	21.19	28.00	35.89	0.0321	0.0282
10	0.04460	0.03157	0.02646	22.42	31.68	37.79		
Solv.	0.04272	0.03196	0.02503	23.41	31.29	39.95	0.0337	0.0277

TABLE 25.—*Barium Chloride in Formamid.*[K; for 15° = 1.58×10^{-5} ; for 25° = 2.02×10^{-5} ; for 35° = 2.45×10^{-5} .]

V	Molecular conductivity.			Dissociation.			Per cent.		Conductivity units.	
	15°	25°	35°	15°	25°	35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
10	30.58	40.00	50.12	70.3	71.6	70.1	0.0308	0.0253	0.942	1.012
50	38.06	49.43	61.90	87.5	88.5	86.6	0.0299	0.0234	1.137	1.157
200	40.38	52.48	65.93	92.9	93.9	92.2	0.0300	0.0256	1.210	1.345
800	43.45	55.82	70.38	99.9	99.9	98.5	0.0285	0.0261	1.237	1.456
1,600	43.48	55.86	71.48	100.0	100.0	100.0	0.0285	0.0280	1.238	1.562

V	Viscosity and fluidity.						Temperature coefficients of fluidity.	
	η 15°	η 25°	η 35°	φ 15°	φ 25°	φ 35°	15 to 25°	25 to 35°
10	0.04941	0.03702	0.02878	20.24	27.01	34.75	0.0335	0.028
Solv.	0.04301	0.03221	0.02510	23.25	31.05	39.84	0.0335	0.0283

TABLE 26.—*Mercuric Chloride in Formamid.*[K, for 15° = 1.30×10^{-5} ; for 25° = 1.65×10^{-5} ; for 35° = 2.03×10^{-5} .]

V	Molecular conductivity.			Dissociation.			Per cent.		Conductivity units.	
	15°	25°	35°	15°	25°	35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
4	0.43	0.59	0.83				0.0372	0.0407	0.016	0.024
10	0.63	0.87	1.27				0.0381	0.0460	0.024	0.040
50	1.09	1.56	2.22				0.0431	0.0423	0.047	0.066
200	1.74	2.53	3.68				0.0437	0.0455	0.076	0.115
400	2.73	4.15	5.82				0.0520	0.0402	0.142	0.167
1,000		134.49								
1,600		101.13								
3,200		75.35								

V	Viscosity and fluidity.						Temperature coefficients of fluidity.	
	η 15°	η 25°	η 35°	ϕ 15°	ϕ 25°	ϕ 35°	15 to 25°	25 to 35°
4	0.04688	0.03527		21.33	28.35			
10	0.04496	0.03376		22.25	29.62			
Solv.	0.04301	0.03221	0.02510	23.25	31.05	39.84		

TABLE 27.—*Cobalt Bromide in Formamid.*

V	Molecular conductivity.			Dissociation.			Per cent.		Conductivity units.	
	15°	25°	35°	15°	25°	35°	15 to 25°	25 to 35°	15 to 25°	25 to 35°
10	27.11	35.35	44.30	60.9	61.4	60.7	0.0304	0.0253	0.825	0.895
50	34.70	45.01	56.56	78.0	78.1	77.5	0.0297	0.0257	1.031	1.155
200	39.00	50.34		87.7	87.4		0.0291		1.134	
800	44.48	57.60	72.95	100.0	100.0	100.0	0.0295	0.0266	1.312	1.535
1,600	41.83	53.96	68.70				0.0290	0.0273	1.213	1.474

V	Viscosity and fluidity.						Temperature coefficients of fluidity.	
	η 15°	η 25°	η 35°	ϕ 15°	ϕ 25°	ϕ 35°	15 to 25°	25 to 35°
10	0.04892	0.03699	0.02867	20.44	27.03	34.88	0.0322	0.0290
Solv.	0.04301	0.03221	0.02510	23.25	31.05	39.84	0.0335	0.0283

In this laboratory, during the past fifteen years, solutions in the following pure solvents have been investigated: Water, methyl and ethyl alcohols, acetone, and glycerol. Among the results of this work are the discovery or confirmation of many relations between the conductivity and viscosity of solutions, the dissociation of the solutes, and the die-

lectric constant, association factors, and viscosities of the solvents.¹ Reference to table 7 (p. 24) shows that formamid is a solvent markedly different from any other pure solvent investigated in regard to the three constants mentioned. The evidence obtained supports and confirms all the relations and conclusions that have been established by Jones and his co-workers, from their investigations with other pure solvents. These relations will be discussed in turn.

The Thomson²-Nernst³ theory is that the forces which hold the atoms together are electrical; hence the solvent having the highest dielectric constant has the greatest dissociating power. The dissociating power of solvents is shown in two ways: first, by comparing the percentage dissociation of solutions having the same normality; second, by comparing the dilutions at which complete dissociation is reached. Compare table 12 with table 28.

TABLE 28.—Potassium Iodide in Water.

V	μ_v	α	Temperature coefficient per cent at 25°–35°.
2	112.8	76.6	1.85
8	120.7	82.0	1.97
2,048	147.2	100.0	2.04

Table 12 shows that the dissociation of the N/2 solution of potassium iodide in formamid is only 71 per cent at 25°. From the viscosity data in table 12, we calculate that the viscosity of the N/2 solution is 12.4 per cent greater than the solvent, while the viscosity of the N/2 solution of potassium iodide in water is known to be less than that of the solvent. From a large mass of evidence, we know that viscosity is by far the largest factor affecting conductivity in solutions in which dissociation is of the same order of magnitude. The conductivity of the N/2 solution in formamid at 25° is 18.67. We can assume, without appreciable error, that if the viscosity of the solvent and the N/2 solution were in the same ratio as in the case of the potassium iodide solution in water, the conductivity of the N/2 solution in formamid would be at least 12.4 per cent larger than the figure given—18.67. Recalculating the dissociation of the potassium iodide-formamid solution on this basis gives 79.4 per cent, compared with 76.6 per cent for the potassium iodide solution in water. This latter figure would be even less, if corrections were made for the fact that the viscosity of an N/2 solution in water is less than that of the solvent, which would be a legitimate correction to make for the purpose of this comparison. Comparing in this way the dissociation of these two N/2 solutions, we find, as would be expected from the Thomson-Nernst theory, *that formamid has the greater dissociating power.*

¹These results have been tabulated and discussed in publications of the Carnegie Institution of Washington, Nos. 170, 180, and 210.

²Phil. Mag., 36, 320 (1893).

³Zeit. phys. Chem., 13, 531 (1894).

Complete dissociation of potassium iodide in formamid is found in the N/200 solution, while in water it is not reached till the N/2048 solution. Therefore, in both respects formamid falls in line with the Thomson-Nernst theory. This relation is confirmed by every salt studied in this investigation for which data for comparison are available. The rubidium salts show the stronger dissociating power of formamid much more than some others that were investigated.

The hypothesis of Dutoit and Aston¹ states that the greater the association factor of the solvent the greater its dissociating powers. Table 7 shows the relation of formamid to other pure solvents in regard to association factors. The correction and comparisons made above, with reference to the Thomson-Nernst theory, are equally applicable in connection with the Dutoit and Aston theory.

Jones and Mahin showed that complete dissociation of lithium nitrate in acetone is not reached even when V is 100,000. The significance of these figures is apparent, if one has in mind the association factors and dielectric constants of formamid, ethyl alcohol, and acetone, given in table 7.

Jones and Veazey's² explanation of the decrease in viscosity produced to the greatest extent by cæsium and rubidium salts, and in a less degree by potassium, ammonium, and other salts, all having very large molecular and atomic volumes, has been of special interest in this investigation. They base their hypothesis on the theory of Thorpe and Rodger, that viscosity is due to the friction between the surfaces of the molecules. If the particles of the solute are larger than those of the solvent, the frictional surfaces and, consequently, the viscosity will be decreased. If the added particles are smaller than those of the solvent, the viscosity will be increased by the addition of the solute. The viscosity of all the concentrated solutions of salts having very large atomic or molecular volumes, has been found to be less than the solvent in the case of all pure solvents, except acetone, which have previously been studied. The viscosity of formamid has, on the contrary, been *increased* by every salt used. The complex formamid molecules HCONH_2 , and its very large association factor (6.18) show that its actual molecule is *larger than that of any other pure solvent used in these investigations*, and the increase in viscosity by the salts named above confirms this conclusion. The following comparison strikingly illustrates this relation. A N/2 solution of rubidium iodide in glycerol *decreases* the viscosity of the solvent 13 per cent, while a N/2 solution of the same salt in formamid *increases* the viscosity of the solvent 12 per cent. This relation will be referred to again in discussing the results of the work with cæsium nitrate and chloride.

¹Compt. Rend., **125**, 240 (1897).

²Amer. Chem. Journ., **37**, 405 (1907); Carnegie Inst. Wash. Pub. No. **80** (1907).

That the percentage temperature coefficients of conductivity increase as the viscosity of the solution increases is a relation that has been brought out by all the investigations in this laboratory. These coefficients for solutions in formamid have the order of magnitude that would be expected from the relation of their viscosities to the viscosities of the same solutions in other solvents. For example, compare the coefficients for solutions of potassium iodide in water, table 28, with those for the same salt in formamid (table 12).

All salts containing water of crystallization were carefully dehydrated at suitable temperatures just before the solutions were prepared. No thermal measurements were made of the heat of solution, but in the case of sodium iodide, which crystallizes with two molecules of water, a marked rise in temperature was noted when the salt dissolved in formamid, which indicated the formation of a solvate. It is well known that solvated salts give higher temperature percentage coefficients of conductivity than non-solvated, because complexes are usually simplified by rise in temperature. In the present investigation, salts crystallizing with water have given the larger coefficients, indicating the formation of solvates analogous to the formation of solvates by the same salts in water and other solvents. To illustrate this relation, let us compare these coefficients for sodium chromate crystallizing with 10 molecules of water (table 10) and cobalt bromide crystallizing with 2 molecules of water (table 27). Also, compare sodium iodide, crystallizing with 2 molecules of water (table 9) with potassium iodide (table 12). The coefficients for the dilute solutions of sodium chromate are probably not reliable for this comparison, as will be explained under the discussion of this salt.

SODIUM CHROMATE.

Table 10 gives the results for sodium chromate. They are of the usual order of magnitude, except for the N/1600 solution. At each temperature the increase in conductivity between the N/800 and N/1600 solutions is 59 per cent, which is probably due to chemical action or decomposition instead of to an increase in ionization.* Formic acid is a strong reducing agent. Formamid may be considered as formic acid in which a hydroxyl has been replaced by an amino group. Both the hydroxyl and amino group are basic; therefore, we might expect from this relationship that formamid would be a reducing agent. The reducing action of formamid will also be discussed with the results for mercuric chloride. Sodium chromate is a strong oxidizing agent; hence, it is not surprising that there should be chemical action between these two compounds when the chromate is in a highly ionized condition, as in a dilute solution. The percentage dissociations have not been calculated, because the conditions just referred to introduce an uncertainty regarding them.

MERCURIC CHLORIDE.

The conductivity of aqueous solutions of mercuric chloride is too small to be measured, but in formamid, on account of its greater dissociating power, the conductivity is measurable and increases as dilution increases in the usual way up to the N/400 solution. The conductivity values for the N/1000, N/1600 and N/3200 solutions clearly result from some decomposition, probably of the solvent. The conductivity of barium chloride at complete dissociation is 55.86 at 25°. The large value 134.49 for the N/1000 solution of mercuric chloride shows that it is not due to dissociation. Assuming that at complete dissociation the conductivity of mercuric chloride would be of the same order of magnitude as of barium chloride, the dissociation of the N/4 solution would be about 1 per cent, increasing to about 7 per cent for the N/400 solution. Silver chloride is precipitated in the N/400 solution by silver nitrate. By standing in the sunlight for a short time, a heavy precipitate of metallic silver is formed, showing again the reducing action of formamid.

To recover the solvent from the mercuric chloride by vacuum distillation required several more distillations than usual. Metallic mercury was found in the receiver after the first distillation, showing again the reducing action of formamid. It is possible that the liberated chlorine formed a salt with the formamid which was easily dissociated, since the conductivity of the first fraction of the distillate was very high and was lowered only a small amount by successive distillations. Repeated distillation, however, yielded the solvent used for the cæsium solutions.

COBALT BROMIDE.

The green, anhydrous cobalt bromide gives a pink solution in formamid as in water. After the determinations were made, a mixture of solutions was distilled to recover the formamid. The mixture contained mercuric chloride and cobalt bromide. As already stated, the mercuric chloride was reduced to metallic mercury. The dry residue in the distillation flask had the brilliant blue color of anhydrous cobalt chloride, showing that the free chlorine from the mercuric chloride had replaced the bromine in the cobalt bromide.

CÆSIUM NITRATE AND CHLORIDE.

For several years past this laboratory has been unable to obtain any cæsium salts for its investigations on conductivity and viscosity. Recently some cæsium sulphate was obtained through the cooperation and courtesy of Prof. James Lewis Howe, of Washington and Lee University. The sulphate was converted into the nitrate and chloride, and the conductivity and viscosity of solutions of these salts were determined. The results are recorded in tables 22 and 23.

A survey of the work on the salts of all the alkali metals shows that conductivity values for the caesium, rubidium, and potassium salts are approximately the same, and for sodium and lithium are less. The same relation is true for the results obtained in aqueous solutions. Dissociation percentage is of the same order of magnitude for all the salts named. The conductivity results, in connection with the dissociation percentage, harmonize with the ionic velocities. For caesium, rubidium, and potassium the relative ionic velocities are 73.6, 73.5, and 70.6, and for sodium and lithium they are 49.2 and 39.8.

The most striking difference between these metals is shown by the atomic volume curve of Lothar Meyer.¹ This function increases by nearly regular steps from 12 for lithium to 72 for caesium. In accordance with the theory of Jones and Veazey,² to which reference has already been made, the percentage increases in the viscosity of the concentrated solutions over the viscosity of the solvent, should be the smallest for caesium salts, and should increase in the following order; caesium, rubidium, potassium, sodium, and lithium. This relation comes out clearly by comparing the figures given in the last column of tables 8 to 27. (Compare these results for caesium and rubidium salts with those for sodium and lithium). The salts of rubidium and caesium increase the viscosity of formamid much less than sodium and lithium salts. The difference in percentages of increase is not so marked as the difference in the atomic volumes of the metal ions. The effect is partially suppressed by other factors. Consider the solution of a binary salt which is 80 per cent dissociated. Every hundred molecules of the salt gives, in solution, 80 anions, 80 cations, and 20 molecules. The 80 cations are only 44.5 per cent of the number of particles in the solution. It is only this 44.5 per cent of cations which have the atomic volume relations referred to above. The molecular volumes do not show this relation, and the atomic volumes of the anions is unknown.

SUMMARY OF RESULTS.

The first six of the conclusions drawn below have been developed or confirmed by the investigations in this laboratory with other pure solvents, and have been shown by this investigation to hold true for formamid.

1. The greater the dielectric constant of a solvent the greater its dissociating power.

2. The greater the association factor of a solvent the greater its dissociating power.

3. The formation of *solvates* with formamid is indicated by those salts that form hydrates with water.

¹Lieb. Ann. Suppl., **7**, 354 (1870).

²Carnegie Inst. Wash. Pub. No. **80** (1907); Amer. Chem. Journ., **37**, 405 (1907).

4. Solvated salts show larger percentage temperature coefficients of conductivity than non-solvated salts.

5. The order of magnitude of percentage temperature coefficients of conductivity is approximately proportional to the viscosity of the solutions.

6. Formamid is the first of the pure solvents studied with reference to the viscosity of solutions, in which none of the salts used produces negative viscosity. A satisfactory explanation of the above fact is apparent, if the very large association factor of the solvent is considered in connection with the theory of Jones and Veazey.

7. In regard to conductivity, dissociation and effect on viscosity of solvent, cæsium salts are very closely allied to rubidium salts.

8. Mercuric chloride is more dissociated in formamid than in water.

CHAPTER III.

RADIOMETRIC MEASUREMENTS OF THE IONIZATION CONSTANTS OF INDICATORS.—I.

BY E. J. SHAEFFER AND M. G. PAULUS.

The radiometric measurements recorded in this paper were made with a very sensitive radiomicrometer and a grating spectroscope. The spectroscope is well known to the chemist, but its use in connection with the radiomicrometer has not, as yet, found an extensive application to the study of chemical problems. This is perhaps due in part to the difficulty in constructing a sensitive and easily controlled radiomicrometer. By means of the grating spectroscope and radiomicrometer, it is possible to study quantitatively chemical reactions involving color changes, and even those not involving such changes, if there are absorption bands in the invisible regions of the spectrum. It will be seen that accurate determinations of very small concentrations of colored components in solutions can be made very rapidly even when two or more such components are present. The structure of the solvent bands and time reactions are among the many other important chemical problems which may be investigated by means of this radiometric apparatus.

PURPOSE OF THIS INVESTIGATION.

In connection with some problems now under investigation in this laboratory, it was desired to secure accurate measurements of the hydrolysis constants of certain salts. The spectroscope and radiomicrometer suggested the indicator method, which is based on the changes in the transmission of light by solutions of indicators when varying amounts of hydrogen or hydroxyl ions are present. It will be shown that by means of these changes the concentrations of very small amounts of hydrogen and hydroxyl ions can be determined. The method obviously involves a knowledge of the ionization constant of the indicator as an acid or as a base. A comparison of the ionization constants of the indicators obtained by several investigators, showed that the recorded values varied widely, not only with different methods, but with the same method. The results for phenolphthalein, in particular, indicate how inaccurate is our knowledge as to the ionization constant of that important indicator. Salm¹ gives the value 8×10^{-10} ; McCoy,² 0.8×10^{-10} . In many cases the results of an individual investigation vary as much as 300 to 400 per cent. A. A. Noyes³

¹Zeit. phys. Chem., **57**, 492 (1907).

³Journ. Amer. Chem. Soc., **32**, 858 (1910).

²Amer. Chem. Journ., **31**, 503 (1904).

has applied the theory of indicators to volumetric analysis, making use of the ionization constants of the various indicators. He expresses the opinion that our knowledge of the ionization constants of the indicators is for the most part inexact and needs to be supplemented by further careful investigation. Stieglitz,¹ McCoy,² and Salm have also recognized the importance of such a study. McCoy, Salm, and in particular Noyes and Bjerrum,³ have already applied the indicator constants to some of the more important problems which the chemist must face in titrating weak acids and bases; and they have shown in certain cases the extent of the error involved in such titrations. It will then be readily seen that it is important to know the ionization constants of the more important indicators, especially of methyl orange and phenolphthalein. In view of these facts, and the value of such ionization constants in many other lines of work involving the use of indicators, it was decided to make a radiometric investigation of this problem. Methyl orange was first studied, and a method was developed through the application of Beer's law, which readily gave the concentration of the yellow azo-base and that of the red quinoid ion. Knowing these values and the hydrogen ion concentration, the hydrolysis constant of methyl orange can be readily calculated. The method employed is different from, and was worked out independently of any other method thus far used in investigating this problem.

HISTORICAL.

The results of a number of preliminary investigations on the ionization constants of various indicators were published in 1904. McCoy, like most of the other investigators who studied this problem, worked calorimetrically, the intensity of the color being judged by the eye. McCoy employed Nessler tubes for this purpose, while others made use of special calorimeters to determine the amount of indicator transformed into its salt by varying amounts of hydrogen or hydroxyl ions. Tables showing roughly the hydrogen ion concentration at which a large number of indicators undergo change in color, have been published by Friedenthal,⁴ Salessky,⁵ Fels,⁶ and Salm.⁷ Nearly all of the early investigators utilized the principle that the ionization constant of an indicator is equal to the hydrogen ion concentration at which it is one-half transformed into its salt. (See Salm and A. A. Noyes.) Salessky, and later Salm, determined the concentration of the hydrogen ions at this point by means of the hydrogen electrode. Criticisms showing how inexact most of these methods are will be found in the separate articles. Salm,⁸ referring to the work previous to 1907, says

¹Journ. Amer. Chem. Soc., **25**, 1126 (1903).

²Amer. Chem. Journ., **31**, 503 (1904).

³Ahr. Versamm., **21**, 1 (1914).

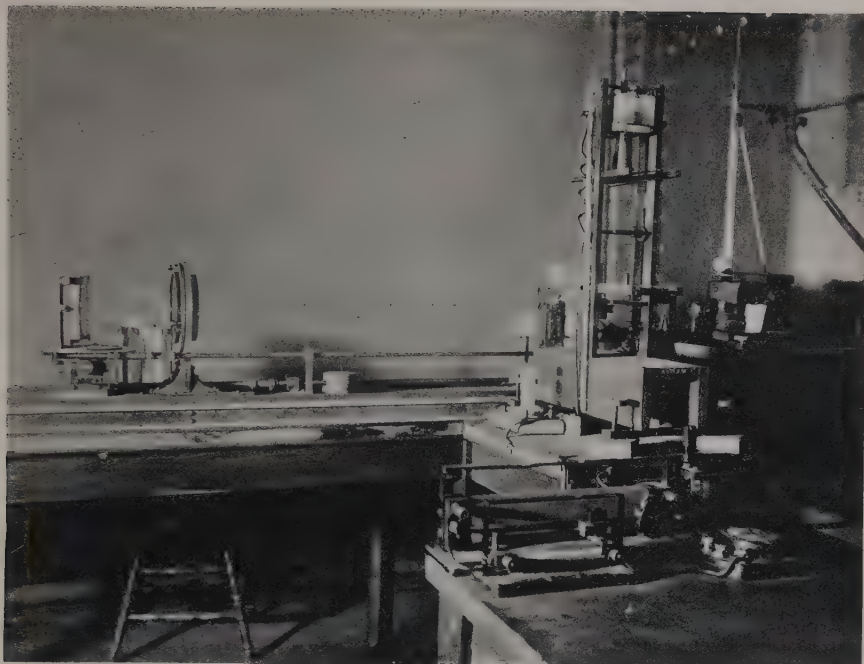
⁴Zeit. Elektrochem., **10**, 113 (1904).

⁵*Ibid.*, **10**, 204 (1904).

⁶*Ibid.*, **10**, 208 (1904).

⁷*Ibid.*, **10**, 344 (1904).

⁸Zeit. phys. Chem., **57**, 490 (1907).



1. Spectroscope without Cover.



2. Radiomicrometer.

that the investigations have been for the most part qualitative, and that with few exceptions the dissociation constants of the indicators are still unknown.

Salm made a more careful study, employing a satisfactory calorimeter to determine when the indicator was one-half transformed into its salt, and like Salessky obtained the hydrogen ion concentration at this point by means of the hydrogen electrode. His results with phenolphthalein illustrate the uncertainty of the values found by his method. Wegscheider¹ proceeded in much the same manner as the others who have used the colorimetric method, and obtained constants for the ionization of phenolphthalein which seem to be in fair agreement with those found by Hildebrand.² Hildebrand's method, involving the use of the spectro-photometer for the estimation of color intensities, is the most exact of all the methods previously employed. His photometric method somewhat resembles the radiometric method which we employed. Rosenstein,³ following essentially the procedure of McCoy, has carried out very carefully a colorimetric investigation of the ionization constant of phenolphthalein, and the effect upon it of neutral salts. He employed the Duboscq type of colorimeter to determine the fraction of the indicator transformed by a known hydrogen ion concentration. As he shows, the ionization constant is equal to the hydrogen ion concentration multiplied by the fraction of the indicator transformed into its salt. When the indicator is a fairly strong electrolyte, *e. g.*, *p*-nitrophenol, its dissociation constant was determined by the conductivity method.

Before we can judge of the absolute value of the results obtained in any radiometric investigation, it is necessary that the radiometric instrument and the other parts of the apparatus used in connection with it, which fulfill several requirements, be taken up in the discussion of the apparatus which follows. In view of the fact that radiometric apparatus has not thus far been extensively used by chemists, it seems desirable that this be discussed in some detail.

Photographs of the assembled apparatus and also of the various parts are given in plate 1, figure 2, and plates 2 and 3 show the assembled apparatus. The long box to the left (plate 1, fig. 2) incloses the spectroscope. The standard which holds the Nernst glower, lenses, sliding carriage, etc., occupies the center, and the tall box to the right incloses the radiomicrometer. Below the standard is shown the rheostat ammeter, etc., for controlling the current supplied to the Nernst glower. Plate 2, figure 1, is a photograph of the apparatus with the covers removed from the spectroscope and the radiomicrometer. To the extreme left is shown the grating and a 4-inch Brashear lens, and at the extreme right is the tube containing the radiomicrometer with the

¹Zeit. Elektrochem., **14**, 510 (1908).

²*Ibid.*, **14**, 351 (1908).

³Journ. Amer. Chem. Soc., **34**, 1117 (1912).

permanent magnet at the bottom. Plate 2, figure 2, is a side view of the radiomicrometer. A larger view of the lens and grating is shown in plate 3, figure 1; an end view of the spectroscope in plate 3, figure 2.

THE RADIOMICROMETER.

The methods employed in the construction of the radiomicrometer and especially of the thermo-junctions, we owe to Professor A. H. Pfund.¹ By means of these methods we were able to build a very satisfactory instrument.

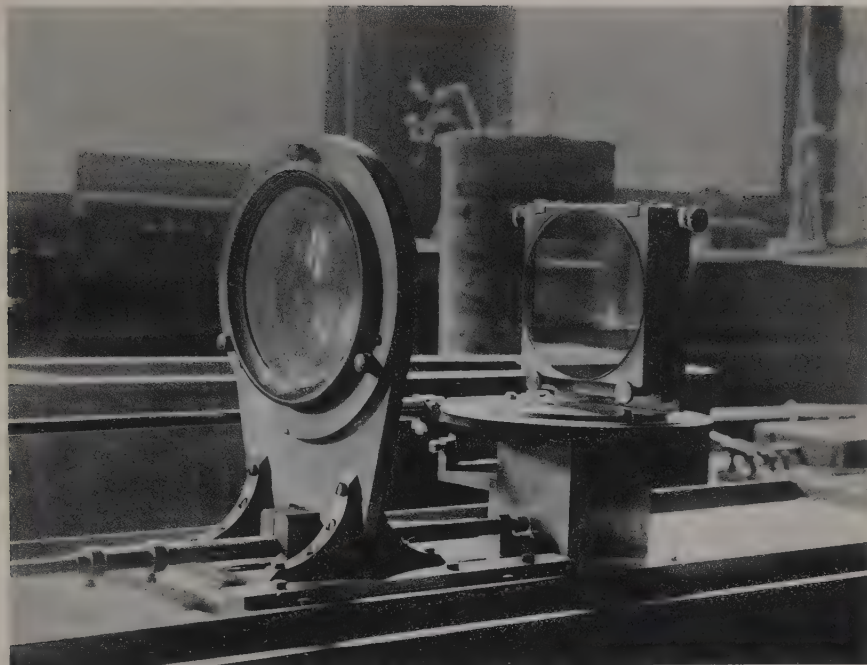
The radiomicrometer previously constructed by Guy² was found to be unsatisfactory for use with the grating spectroscope. Its sensibility, according to a recent test, was 2 per square millimeter of exposed vane, candle and scale being at a meter's distance. The full period of this instrument was, however, very short, being only 8 seconds. His radiomicrometer could have been made about as sensitive as the one constructed for this work, by using a longer and finer quartz fiber and making the full period about 20 seconds. However, as this instrument was not equipped with a compensating junction, and as its drift due to this cause, had proved so troublesome in the work of the previous year, it was decided to construct a new radiomicrometer.

Briefly, the radiomicrometer consists of a thermo-electric junction attached to a loop of non-magnetic wire. The whole system is suspended by a quartz fiber in a glass tube. A strong magnetic field surrounds that portion of the tube inclosing the loop of wire. Radiant energy falling upon the blackened junction is converted into electrical energy. In proportion to the amount of energy received by the junction, the suspended system turns through a definite angle in the magnetic field, the loop tending to set itself at right angles to the lines of force. The deflection or turn is given by means of a mirror attached to the suspended system.

The essential parts of the radiomicrometer are shown in figure 6, which represents the type of compensating junction that was constructed and used. It is fastened to the loop of copper wire w at c and c' , as shown in figure 6. To support the loop of wire small glass rods are placed at h and h' . A light mirror is attached to h at m . A quartz fiber, f , is fastened to the end of the glass rod h , and to the brass stopper S . The whole system is then set in the glass tube T , having two windows l and p . The lens l focuses the reflected light from the mirror m , on a glass scale. At p is inserted a plane-glass window 1 mm. thick. The beam of light which is to be measured passes through this window before falling on the junction. The magnetic field is placed between l and p .

¹Phys. Rev., **34**, 228 (1912); Phys. Zeit., **13**, 870 (1912).

²Carnegie Inst. Wash. Pub. No. **190**, 30 (1913).



1. Lens and Grating of Spectroscope.



2. Spectroscope end View.

The wire loop was made of a very fine specimen of No. 36 copper wire, furnished by Leeds and Northrup. Pure nitric acid was used to dissolve the surface of the wire, which was very likely to be contaminated with various magnetic materials. That this wire must have been very pure is shown by the behavior of the completed instrument. As regards purity, a still better specimen of silver wire was obtained from Weston; but unfortunately none of the junctions attached to this silver wire was sufficiently sensitive for our purpose.

The alloys used for the construction of the thermo-junction were of the composition recommended by Hutchins.¹ Figure 6 of the sketch gives an enlarged view of the junction. It will be noticed that it consists of two thermo-electric junctions A and B, which compensate each other. When the same beam of light falls on both junctions, each sends equal amounts of electrical energy through the loop of non-magnetic wire w , but in opposite directions. Hence, it follows that for exact compensation there should be no turn of the suspended system. In actual operation the beam of light energy which is to be measured is focused on one of the junctions. This arrangement of junctions is quite essential in any sensitive radiomicro-meter where a constant zero-point is required; and it is only in this way that the effects of temperature changes and stray sources of light can be eliminated.

The two arms represented by a and a' in figure 6 have the composition 97 parts bismuth and 3 parts antimony. The composition of b is 95 parts bismuth and 5 parts tin. These metals are quite pure and the strips used are very thin. Junction A is formed by sealing strip a to strip b , and junction B is formed by sealing strip b to strip a' . R and R' are the receiving surfaces, or so-called vanes, cut from very thin tin foil, and soldered to junctions A and B, respectively. These vanes each have an area of 4 sq. mm., and are coated with lampblack to prevent radiation of light energy. It was found that the action of an acidified solution of antimony chloride on the tin foil produces a black receiving surface. Theoretically, it appears that such a metallic receiving surface should be more effective than lampblack. However, none of the junctions having the antimony receiving surface was sufficiently sensitive to determine whether or not its use is to be preferred to that of lampblack. Greater sensibility can be obtained with a single junction than with a compensating one, since in the former

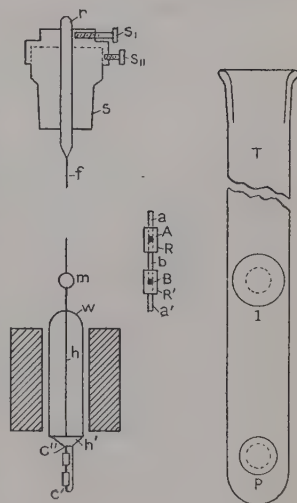


Fig. 6.

¹Sill. Journ., 48, 226 (1894).

we have but one seal and two metal strips. This follows from the fact that the sensibility of the radiomicrometer is materially increased when the resistance of the junction is made more nearly equal to that of the wire loop. However, the advantages to be derived from the compensating type of junction are well worth the sacrifice in sensibility.

It is very important that the weight of the junction be kept as small as possible, not only to lessen the weight of the suspended system, but especially to reduce the heat capacity of the junction to a minimum. A small heat capacity insures a quick-acting suspension, and one which will more rapidly return to the zero-point. That the mass of material in the junction is very small can be seen from the fact that the actual weight of one of the completed compensating junctions was 2.9 mg.

The quartz fiber¹ was obtained from molten quartz by means of a bow-and-arrow arrangement. The total length of this fiber is nearly 30 cm. A long fiber materially aids in eliminating vibrations. This is most essential, especially when the work necessitates small deflections. The period and sensibility of the radiomicrometer depend in a large measure on the proper selection of the quartz fiber.

The plane mirror *m* (fig. 6) is very thin and has an area of about 20 sq. mm. Directly in front of it is the lens *l*, having a focal length of 12 feet. By means of this arrangement the image of a lamp filament could be sharply focused on a glass scale about 12 feet distant from the mirror; and it is on this scale that the deflections as given by the radiomicrometer are noted.

The torsion-head stopper *s*, made of brass and tightly ground into the glass tube *T*, serves the purpose of making adjustment. By means of it the suspended system can be made to occupy any position in the magnetic field, and the whole system can be raised or lowered without danger of breaking the very fragile suspension. The torsion-head stopper contains a brass rod *r* and the two screws *s*₁ and *s*₂ for making the above adjustments.

The glass tube *T*, in which the whole system is suspended, is about 45 cm. in length. To it is attached the lens *l*, previously referred to, and the glass window *p*, through which the beam of light is directed either to junction *A* or to junction *B*.

The glass tube surrounding that portion of the suspended system to which the thermo-junction is attached was insulated from temperature changes and air drafts by a layer of fine lead shot and wool fiber. To prevent stray sources of light and air drafts from reaching the radiomicrometer, it was inclosed in a wooden box covered with painted canvas.

That the image on the scale should remain steady at a focal distance of 12 feet, it is necessary to shield the radiomicrometer very carefully from the usual vibrations of the building. The long quartz fiber aided

¹Dr. C. W. Hewlett has very kindly supplied us with several satisfactory fibers.

materially in this respect. Between the leveling stand of the radiomicrometer and the base on which it rested, various insulating materials were introduced at six points to absorb vibrations.

The completed radiomicrometer, candle and scale being at a meter's distance, gave a deflection of 20 cm., the half-period being nearly 10 seconds. In making this determination of the sensibility of the instrument the radiation was passed through a glass window 1 mm. thick, and the tube containing the suspension was not evacuated. Evacuating the tube and passing the radiation through a rock-salt window would increase the sensibility about six times, and the period would become somewhat shorter.

Since the receiving vane has an area of 4 sq. mm., the sensibility per square millimeter of exposed vane is 5, and the full period 20 seconds. When making this determination, owing to the difficulty of properly shielding the junction not in use but serving as compensator, it is thought that the value of 5 for the sensibility is somewhat low. Practically every junction that was tested showed that the sensibility was approximately one-fourth of the whole period in seconds. The sensibility value as given by the candle has but little meaning, owing to the varying intensity of the light emitted. The light from the Nernst glower, burning at 0.8 ampere and 120 volts, dispersed into the visible first-order spectrum 6 inches long at slit s_1 of the spectroscope, gave at $\lambda = 0.95\mu$ a deflection of 250 mm. when focused on the junction of the radiomicrometer. Both slits are 1 mm. in width, and the scale 12 feet from the mirror. Considering the high resolving power of the grating, it will be seen that our radiomicrometer is very satisfactory, both as regards sensibility and period. It enabled us to make quantitative measurements of radiant energy from $\lambda = 0.4\mu$ to $\lambda = 2.0\mu$.

For the same source of light energy, the radiomicrometer always gave the same deflection and returned quickly to zero, showing that our efforts to eliminate magnetic materials from the wire loop had been very successful. The conduct of the completed instrument has demonstrated that the suspended system is very free from paramagnetic disturbances. The diamagnetic materials composing the junction were all arranged at right angles to the lines of force of the magnetic field, and in this way diamagnetic disturbances were reduced to a minimum. The use of the radiomicrometer has shown that the heat capacity of the junction is sufficiently low to be within the desired limit. The compensating junction and its insulation from temperature changes practically removed any drift of the zero-point. The zero-point for weeks at a time would not drift more than 10 cm. on either side of the zero. In case there was any drift during the measurements, it was always very slight and the proper correction could easily be applied. The insulation from vibrations made the reflected beam upon the scale fairly steady, even when there were rather violent disturbances in the

building. There is every reason to suppose that the scale could be read to about 0.25 mm. when the building was quiet. Duplicate readings under ordinary conditions nearly always agreed to within 0.5 mm.

THE SPECTROSCOPE.

The grating spectroscope was designed and built in the Physical Laboratory under the direction of Professor John A. Anderson. The use of such a spectroscope presents two especially desirable advantages. First, the position of regions of absorption can be very accurately determined; second, due to its high resolving power, the structure of even the very narrow absorption bands and some absorption lines can be studied in detail. The spectroscope is so constructed that either the photographic plate or any of the radiometric instruments can be used with it. The use of the radiomicrometer enables us to determine not only the actual positions of regions of absorption, but also to make quantitative measurements of the light transmitted by a solution for a wide range of wave-lengths. The deflections of the radiomicrometer give an accurate measure of the relative intensities of the different absorption bands, and of the different parts of the same bands. It will thus be seen that the radiometric method has distinct advantages over the photographic, which is chiefly useful in determining the positions of regions of absorption and the general characteristics of the visible spectrum as transmitted by the solutions. Moreover, the photographic plate is only sensitive from $\lambda = 0.2\mu$ to $\lambda = 0.76\mu$, whereas, with the radiomicrometer and the apparatus used in this work, quantitative measurements of absorption could be made from $\lambda = 0.4\mu$ to $\lambda = 2.0\mu$, using slits only 1 mm. in width. Considering the high dispersion that could be obtained with the 4-inch grating, this width of slit gives a very pure spectrum.

The plane 4-inch grating with which the spectroscope is equipped was ruled by Anderson; and the ruling is of such a character that a very bright first-order spectrum is produced. This is quite essential for radiometric measurements in the visible region of the spectrum. Energy measurements were made in both first-order spectra, one being on each side of the central image. The spectrum on one side was found to be somewhat more intense, and therefore this brighter side was used.

If either the intensity of the light source or the sensitiveness of the radiomicrometer exceeds certain limits, it is possible that light energy from the second-order spectrum will vitiate the energy measurements made in the first-order spectrum. This will be readily seen if we consider that wave-length of light $\lambda = 0.35\mu$ of the second order overlaps wave-length of light $\lambda = 0.7\mu$ of the first order, etc. Therefore, it was desired to know if, with a Nernst glower burning at 0.8 ampere and 120 volts, the second-order spectrum had sufficient energy to be

detected by the radiomicrometer. If such proved to be the case, it would be found necessary to introduce color screens to eliminate the light energy from the second-order spectrum. That the first-order spectrum can be regarded as pure is shown by the following considerations:

Glass cuts off all wave-lengths of light beyond $\lambda = 0.35\mu$. Since the glass in the path of the light is of considerable thickness, the first-order spectrum is not contaminated with any light from the second-order spectrum as far out as $\lambda = 0.7\mu$ of the first order. A solution of copper sulphate is entirely transparent to all wave-lengths of light shorter than $\lambda = 0.6\mu$. A 10 mm. depth of a saturated solution of copper sulphate shows complete absorption beyond $\lambda = 0.6\mu$. Using the above solution of copper sulphate, radiometric measurements were made from $\lambda = 0.4\mu$ to $\lambda = 1.3\mu$. Beyond $\lambda = 0.6\mu$ the solution of copper sulphate is entirely opaque, and therefore no evidence of light energy from the second order was obtained as far out as $\lambda = 1.3\mu$. It has already been shown that the first-order spectrum is pure up to $\lambda = 0.7\mu$, and the above shows that the light from the overlapping second-order spectrum does not contain a sufficient amount of energy to be detected by the radiomicrometer as far out in the infra-red as $\lambda = 1.2\mu$ of the first-order spectrum. The radiometric measurements of the dissociation constants of the indicators were all made between $\lambda = 0.5\mu$ and $\lambda = 0.6\mu$, and in this region the first-order spectrum is absolutely pure.

The drumhead which rotated the grating through definite angles is a large one, its diameter being 4 inches. It is attached to a very carefully constructed screw, so designed that each complete revolution changes the wave-length of light falling on the slit by approximately 500 Å. u. The drum contains 500 divisions, and, all things considered, it is quite probable that the wave-length settings are accurate to within one or two Ångstrom units.

The spectroscope is of the Littrow mounting, the same lens serving both as telescope and collimator. It is provided with two 4-inch lenses made by Brashear. One lens has a focal length of 72 inches and is intended for photographic work. The other, and the one which was used in this work, has a focal length of 30 inches. With this lens, the visible first-order spectrum at slit s_2 has a length of over 6 inches. Provision has also been made for the mounting of a large glass prism on the grating table, and it is purposed to use this prism when an intense first-order spectrum is desired, rather than a spectrum which is widely dispersed. Had we not been successful in constructing a very sensitive radiomicrometer, it would have been necessary to make frequent use of the glass prism.

The spectroscope was placed in a brass box, blackened on the inside, which prevented stray sources of light from reaching the grating. The slits were of the bilateral type.

The calibration curve for the grating and drumhead was calculated from the known grating space, by means of the equation

$$\lambda = 33,866.7 \sin \frac{3000 \cdot T + 6R}{3500}$$

where T is the number of complete turns of the screw which rotates the grating and R is the reading on the drum. The calibration was also effected by observing the positions of various mercury, sodium, and lithium lines. It was decided that the calculated values are more accurate than the observed; and, accordingly, the dispersion curve based on the calculated values was used.

SOURCE OF LIGHT.

A Nernst glower served as the source of light, the electrical energy being supplied by a series of storage batteries. By means of a rheostat the light intensity could be kept quite uniform. The glower was protected from air drafts by means of a box of asbestos wood. Provision was made for the mounting of a nitrogen lamp¹ when it was desired to secure large deflections of the radiomicrometer for wave-lengths of light shorter than $\lambda = 0.5\mu$.

THE CELLS.

A very important part of the equipment is the cells which contain the solutions to be investigated. There are two cells made as nearly alike as possible. The cell consists of two brass cylinders which closely telescope into one another. One end of each cylinder is closed by a glass plate held in position by Wood's fusible metal. The four glass ends used in the cells are all of the same thickness, *i. e.*, 2 mm. Their surfaces are plane, and are parallel to within 5 wave-lengths of light. It is difficult to set these plates in the brass cylinder with Wood's fusible metal, without warping them and destroying their plane-parallelism. The character of the interference fringes which the plates gave with the mercury arc determined when they were correctly adjusted. A fine thread was "chased" on the outer cylinder. This thread carried a nut which, when turned, raised or lowered the inner cylinder a definite amount. Each complete revolution of this nut changed the distance between the plates by 1 mm. The nut contained 100 divisions, and by means of this arrangement we could readily adjust the depth of the solutions to within less than 0.01 mm. Each cell was then filled with a layer of water 5 mm. in depth, and the deflections given by the radiomicrometer were noted for a light source of uniform intensity throughout the whole region of the spectrum under investigation, namely, from $\lambda = 0.4\mu$ to $\lambda = 2.0\mu$. The deflections

¹Dr. W. R. Whitney, of the General Electric Company, very kindly supplied us with two lamps of special design to be used for this purpose.

should agree with each other very closely for all wave-lengths of light if the cells are optically identical. Having made sure that the cells are optically identical, they were heavily plated with gold to remove any possibility of the solutions attacking the metals of the cell. It is very important to keep the solutions perfectly clear when measurements are being made, and the glass ends must be maintained absolutely clean. Table 29 shows the optical identity of the two cells. Under cell A and cell B are given the actual radiomicrometer deflections for various wave-lengths of light.

TABLE 29.—*Comparison of the two cells.*

$\lambda = \text{\AA. U.}$	Cell A.	Cell B.	$\lambda = \text{\AA. U.}$	Cell A.	Cell B.
4546	4.0	4	8029	125.0	125.0
4797	8.2	8.2	8275	127.0	127.5
5047	14.2	14.5	8520	129.0	129.0
5298	22.0	22.5	9009	129.5	130.0
5548	31.5	31.5	9497	115.5	115.0
5797	41.5	41.7	9982	105.5	106.0
6046	50.5	50.5	10465	113.5	114.0
6295	60.7	60.7	10946	108.5	108.0
6543	70.5	71.2	11424	69.0	69.0
6792	86.7	86.5	11900	51.5	52.0
7041	100.5	100.0	12373	56.0	56.0
7290	107.7	107.7	12843	53.5	54.0
7536	114.0	114.5	13314	34.0	34.0
7784	120.5	120.5	13775	11.0	10.7

Having discussed the principal parts of the apparatus, viz, the radiomicrometer, spectroscope, source of light, and the cells, and having shown how they meet the requirements demanded by work of this character, it is desirable to consider next the general arrangement of the various parts.

ARRANGEMENT OF APPARATUS.

The Nernst glower, lenses, prisms, and carriage for the cells were mounted on an upright steel standard placed by the side and near the end of the spectroscope next to the radiomicrometer. Parallel light from the Nernst glower was made to pass, by means of a carefully adjusted sliding carriage, first through one cell and then through the other. The two cells could thus be made to occupy the same position in the path of the light. The light transmitted by the solutions contained in the cells was then deflected by means of a right-angle prism and focused on the slit of the spectroscope s_1 . Inside of the box inclosing the spectroscope, and directly in the rear of slit s_1 , was placed another right-angle prism which reflected the light through a 4-inch lens to the grating. The dispersed light was reflected back through this same lens and focused on the slit of the spectroscope s_2 . The light that emerged through slit s_2 was again brought to a focus on the junc-

tion of the radiomicrometer. By turning the drumhead of the spectro-scope to the proper points, we could then determine quantitatively the light transmitted by any solution for all wave-lengths of light between $\lambda = 0.4\mu$ and $\lambda = 2.0\mu$.

THE DIFFERENTIAL METHOD.

It was desired to measure the absolute percentage transmission of 20 mm. of solution. This was done by a differential method which eliminated corrections for reflection from the glass ends, and differences in the refractive index of the glass and the solutions. The method of procedure is as follows: Cell A is filled with 21 mm. of solution; cell B with 1 mm. of solution. Light of unvarying intensity I_0 was then passed through cell A, and the intensity of the transmitted light I_I was measured by means of the radiomicrometer. As soon as possible, cell B was made to occupy the same position formerly occupied by cell A, and the intensity of its transmitted light I_{II} was determined. The deflection produced when cell A was in the path of light, divided by that given when cell B occupied the same position, determines the absolute percentage transmission for 20 mm. of solution; or, in other words, I_I/I_{II} is the value desired. The justification for this procedure is seen from what follows.

If the depth of solution under investigation is l , the intensity of the incident light I_0 , and that of the transmitted light I , we have the following relations for depths of solution l' and l'' :

$$I_I = I_0 e^{-kl'} \quad (a)$$

$$I_{II} = I_0 e^{-kl''} \quad (b)$$

Dividing a by b we have

$$I_I/I_{II} = e^{k(l''-l')} \quad (c)$$

But the actual percentage transmission of the same solution of depth $l' - l'' = l$ is given by

$$I/I_0 = e^{-k(l'-l'')} = e^{-k(l''-l')}, \text{ or } I_I/I_{II} = I/I_0 \quad (d)$$

THEORETICAL DISCUSSION.

The Ostwald¹ theory of indicators, explaining first the cause of color, and second the difference in sensitiveness of various indicators towards different acids and bases, has been found to be inadequate. Concerning the latter, which is by far the most important side of the indicator question, the Ostwald interpretation is substantially correct. But in consideration of well-known relations between the color and structure of organic compounds, and of the researches of Bernthsen,² Nietzi and Burekhart,³ Hantzsch,⁴ and others, it has been found neces-

¹Lehrbuch der all. Chem., **1**, 799 (1891).

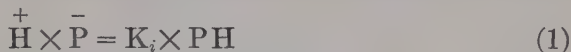
²Chem. Zeit., 1956 (1892); also Friedländer: Ber. d. deutsch. chem. Gesell., **26**, 172, 2258 (1893).

³Ibid., **30**, 175 (1897).

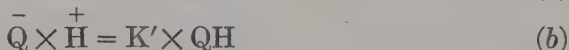
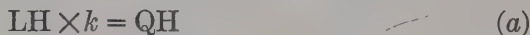
⁴Ibid., **32**, 583, 3085 (1899).

sary to modify the Ostwald view as to the cause of color. The facts and relations brought out by these investigations have been correlated and interpreted by Stieglitz¹ in the so-called chromophoric theory of color. A. A. Noyes², in a quantitative application of the theory of indicators to volumetric analysis, has also fully explained the significance of the chromophoric theory. According to this theory it is necessary to consider an indicator solution as containing a mixture of two tautomeric substances of different structural types. The ionization constants of the two forms, and the equilibrium relations between them, are such that when the indicator exists as a slightly ionized acid or base, one form is present in greatly predominating quantity. The other form largely predominates when the indicator exists as a highly ionized salt.

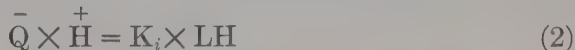
Considering phenolphthalein, the ionization constant K_i , according to the Ostwald conception, is expressed by the simple equilibrium equation



The chromophoric theory, as Stieglitz³ has shown, requires two such equations, (a) and (b):



where k is the stability constant expressing the equilibrium relation between the two tautomeric acids. The acid represented by LH is assumed to be a pseudo- or an extremely weak acid; and that by QH is the true acid. Its ionization constant K' is of such a magnitude that the quinoid salt is formed in greatly predominating quantity in the presence of alkalis, the stability constant k acting so as to maintain the equilibrium relation between the two tautomeric acids. The ionization constant for phenolphthalein is the product of the stability constant k , and the ionization constant K' of the acid QH; or, combining a and b and incorporating k and K' into K_i we have



The above equations illustrate the fundamental differences between the two color theories; and accepting the Stieglitz interpretation of K_i according to equation 2, the theory underlying the calculation of the dissociation constant of methyl orange from radiometric measurements will be discussed.

Methyl orange is in reality a weak base. Noyes⁴ has deduced a general expression for the equilibrium relations of any pair of tautomeric bases and their ions. This deduction involves three fundamental

¹Journ. Amer. Chem. Soc., 25, 1112 (1903).

²*Ibid.*, 32, 815 (1910).

³*Ibid.*, 32, 858 (1910).

⁴*Ibid.*, 32, 818 (1910).

equations. Expressing the equilibrium relation k , between the quinoid and azo-base, it being understood that the symbols represent gram-molecular or gram-ionic concentrations, we have

$$\frac{\text{QOH}}{\text{AzOH}} = k \quad (3)$$

The quinoid base and the azo-base are also in equilibrium with their ions, according to 4 and 5:

$$\frac{\overset{+}{\text{Q}} \times \bar{\text{OH}}}{\text{QOH}} = K_{\text{QOH}} \quad (4)$$

$$\frac{\overset{+}{\text{Az}} \times \bar{\text{OH}}}{\text{AzOH}} = K_{\text{AzOH}} \quad (5)$$

Multiplying 3 by 4 and adding 5 to the product, we have

$$\frac{\overset{+}{\text{Q}} \times \bar{\text{OH}} + \overset{+}{\text{Az}} \times \bar{\text{OH}}}{\text{AzOH}} = k \times K_{\text{QOH}} + K_{\text{AzOH}} \quad (6)$$

and substituting in the denominator for AzOH its value $\frac{\text{AzOH} + \text{QOH}}{1 + k}$ it follows that

$$\frac{\overset{+}{\text{Q}} \times \bar{\text{OH}} + \overset{+}{\text{Az}} \times \bar{\text{OH}}}{\text{AzOH} + \text{QOH}} = \frac{k \times K_{\text{QOH}} + K_{\text{AzOH}}}{1 + k} \quad (7)$$

Letting the above equal K_i , we have

$$\frac{\bar{\text{OH}}(\overset{+}{\text{Az}} + \overset{+}{\text{Q}})}{\text{AzOH} + \text{QOH}} = K_i \quad (8)$$

Noyes has called attention to the fact that for a satisfactory two-color indicator such as methyl orange, the sum of the two tautomeric bases ($\text{AzOH} + \text{QOH}$) must be substantially equal to AzOH ; and that the sum of the two ions ($\overset{+}{\text{Q}} + \overset{+}{\text{Az}}$) must be substantially identical with $\overset{+}{\text{Q}}$. It therefore follows that

$$\frac{\bar{\text{OH}} \times \overset{+}{\text{Q}}}{\text{AzOH}} = K_i \quad (9)$$

where K_i expresses the equilibrium relations of the two tautomeric bases and their ions, and is substantially the equation derived by Stieglitz.¹

Combining equation 9 with that of the ion product of water, $\overset{+}{\text{H}} \times \bar{\text{OH}} = K_w$, we get

$$\frac{\overset{+}{\text{H}} \times \text{AzOH}}{\overset{+}{\text{Q}}} = \frac{K_w}{K_i} = K_{(\text{hydrolysis})} \quad (10)$$

which is in reality the familiar equation of Walker² $\left(\frac{\text{acid} \times \text{base}}{\text{salt}} = k \right)$.

¹Journ. Amer. Chem. Soc., **25**, 1112 (1903).

²Zeit. phys. Chem., **4**, 324 (1889).

Having determined the hydrolysis constant according to equation 10, the ionization constant K_i of methyl orange as a base can readily be obtained. The procedure, then, is to determine by radiometric measurements, the concentrations of $\overset{+}{Q}$, $\overset{+}{H}$, and AzOH in solutions of methyl orange containing varying amounts of these constituents. A method was developed whereby the concentration of the quinoid ions $\overset{+}{Q}$ in equation 10 could be determined from the light transmitted by the indicator solutions. The percentage transmissions for these solutions were given by the radiomicrometer deflections. The method will be made clear by the following theoretical considerations applied to methyl orange.

If we consider light to pass through an absorbing solution of depth l , the solvent itself having no absorption, the rate of change of intensity dI is given by

$$dI = -kI dl \quad (11)$$

The constant k depends only on the wave-length of light and the nature of the absorbing medium. If I_0 denotes the intensity of the incident light, then, when $l = 0$, $I_0 = I = \text{constant}$. Integrating, the intensity of the transmitted light I , given by an absorbing solution of depth l , and concentration c , is

$$I = I_0 e^{-klc} \quad (12)$$

If the solution has a second absorbing component, the light transmitted by it will be

$$I_I = I_0 e^{-k'l'c'} \quad (13)$$

Since the total transmission is the product of the separate transmissions, we have for the actual percentage transmission of a solution containing two absorbing components such as methyl orange

$$I/I_0 = e^{-klc - k'l'c'}; \text{ or } \ln (I/I_0) = -klc - k'l'c' \quad (14)$$

Since the depth of solution was maintained constant (20 mm.), the above equation becomes

$$\ln (I/I_0) = -Kc - K'c' \quad (15)$$

Applying this equation to methyl orange, let c represent the concentration of the quinoid salt or Q in equation 10, and c' that of the azo-base. If T is the total quantity of methyl orange in solution, then $c' = (T - c)$; or, since a dibasic acid was used, viz, sulphuric acid, $c' = (T - 2c)$. When a pure solution of methyl orange is slightly acidified with sulphuric acid, and not all of the azo-base converted into the quinoid salt, both c and c' are present. The light transmitted by such a solution will be:

$$\ln (I/I_0) = -Kc - K'(T - 2c) \quad (16)$$

In a pure aqueous solution of methyl orange, or one containing an excess of alkali, $c = 0$, therefore, equation 15 reduces to:

$$\ln (I/I_0)' = -K'c' = -K'T \quad (17)$$

If to a solution of methyl orange sufficient sulphuric acid is added to convert all of the azo-base into the quinoid salt and completely suppress hydrolysis, $c' = 0$, and equation 15 becomes

$$\ln (I/I_0)'' = -Kc = -KT/2 \quad (18)$$

From equations 16, 17 and 18, K and K' can be eliminated, and solving for c we obtain:

$$c = \frac{T[\ln (I/I_0) - \ln (I/I_0)']}{2[\ln (I/I_0)'' - \ln (I/I_0)']} \quad (19)$$

In the above equation $(I/I_0)'$ is the percentage transmission for the solution of pure methyl orange for some given wave-length of light; $(I/I_0)''$, the percentage transmission of the solution containing an excess of acid for the same wave-length, and (I/I_0) the percentage transmission for the same wave-length of the solution whose quinoid salt concentration c is to be determined.

Returning now to the fundamental hydrolysis equation for methyl orange previously derived:

$$\frac{\overset{+}{H} \times \text{AzOH}}{Q^+} = \frac{K_w}{K_i}$$

we can readily insert the proper values, knowing the total concentration of methyl orange T , and having determined by radiometric means the quinoid salt concentration c . Q is equal to $2c$. $\text{AzOH} = c' = T - 2c$. $\overset{+}{H}$ is given by $2(T' - c)$, where T' represents the total quantity of acid added. It is assumed that the dissociation of these extremely dilute solutions is practically complete. The sulphonic acid group can have but little effect on the hydrogen ion concentration, since benzenesulphonic acid¹ is as strong as sulphuric acid, being dissociated at 25° to the extent of 90 per cent for a dilution $v = 32$. As Stieglitz² has pointed out, the whole behavior of methyl orange is that of a very weak base, and the elimination of the sodium sulphonate group from it leaves dimethylaniline azobenzene, which shows all the characteristics of methyl orange as an indicator.

It will be noticed from equation 10 that it is necessary to know the ionization constant for water before the constant for the indicator can be calculated from its hydrolysis constant. The generally accepted value of K_w at 25° is 1.2×10^{-14} . It was desired to know the value of the constant at 20°, since, unless otherwise stated, it was at this tem-

¹Carnegie Inst. Wash. Pub. No. 170, 128 (1912).

²Journ. Amer. Chem. Soc., 25, 1117 (1903).

perature that all measurements were made. Owing to the large value of the heat of ionization of water, the value of its ionization constant is much less at 20° than at 25°. Just what this change is may be calculated from the well-known Van't Hoff formula

$$\ln \frac{K_1}{K_2} = \frac{q (T_2 - T_1)}{R(T_2 \times T_1)} \quad (20)$$

where K_1 and K_2 represent the ionization constants for water at temperatures T_1 and T_2 . R_1 is the gas constant, which equals 1.986 calories per degree, and q is the heat of ionization of water or 13,700 calories. Inserting these values in equation 20, $K_w = 0.81 \times 10^{-14}$ at 20°. This value was used for the calculation of the ionization constants of both methyl orange and phenolphthalein.

EXPERIMENTAL WORK ON METHYL ORANGE.

Before discussing the tables showing the results of the calculations based on the above deductions, it will perhaps be of interest to consider a few of the more important results of the preliminary work on methyl orange. Two mother solutions of known concentrations were prepared, the one being methyl orange and the other sulphuric acid. All solutions were made up at 20°, and carefully purified substances dissolved in conductivity water were employed in all cases. A number of test solutions were prepared from the mother solutions, all of which contain equal amounts of methyl orange but different amounts of sulphuric acid. The volume of each solution was 100 c.c. The solutions thus presented a series of color shades, ranging from yellow to deep red. The percentage transmissions I/I_0 , were taken with a 20 mm. depth of each solution for the same 4 or 5 wave-lengths of light. The region of the spectrum to be studied is given by the ascending arm of the transmission curve for methyl orange. This region for the above-named indicator is between $\lambda = 0.56\mu$ and $\lambda = 0.59\mu$. The radiomicrometer deflections in this region are necessarily small, and certain variations which appear in the data can be explained in a large measure as due to the vibrations of the building, which often prevented accurate readings.

Special attention is called to a solution of methyl orange containing an excess of alkali, and another solution containing an excess of acid. Equation 19 shows that the calculation of c depends not only on the percentage transmission of the solution in question, but also on the percentage transmission for a solution in which all of the methyl orange exists as the azo-base, and one in which all of the indicator has been converted into the quinoid salt. It is thus necessary to know if any alkali must be added to convert all of the methyl orange into the azo-base and to prevent hydrolysis; and also how much acid is required to form the quinoid salt and to suppress hydrolysis completely. Furthermore, the stability of these solutions must be considered.

Table 30 shows that in a pure aqueous solution of methyl orange there is no appreciable hydrolysis, and that practically all of the indicator exists as the azo-base. It is, therefore, not necessary to add alkali in determining the value of $(I/I_0)'$ in equation 19. The volume of all solutions used in table 30 was 100 c.c. and each solution contained the same amount of methyl orange.

TABLE 30.
[I/I_0 for depth of solution = 20 mm.]

$\lambda = \text{\AA. U.}$	Methyl orange in pure water.	Methyl orange plus 1 c.c. N sodium hydroxide.	Methyl orange plus 2.5 c.c. N sodium hydroxide.
5648	70.3	71.2	70.5
5698	79.3	78.8	79.0
5748	84.6	86.0	84.8
5797	90.0	90.0	88.5
5847	91.4	92.2	90.0

Table 31 gives results for three solutions of methyl orange, each containing an excess of acid and the same amount of indicator diluted to 100 c.c. It shows that 0.2 c.c. of the acid is sufficient to convert all of the azo-base into the quinoid salt and completely to suppress hydrolysis.

TABLE 31.
[I/I_0 for depth of solution = 20 mm.]

$\lambda = \text{\AA. U.}$	Methyl orange plus 0.2 c.c. concentrated sulphuric acid.	Methyl orange plus 0.5 c.c. concentrated sulphuric acid.	Methyl orange plus 1.0 c.c. concentrated sulphuric acid.
5698	15.2	15.2	16.6
5723	20.2	20.1	20.1
5748	30.7	31.2	31.9
5773	39.5	39.2	38.8
5797	48.7	49.2	48.1
5823	55.0	53.8	55.3
5847	61.4	62.6	63.2

Stable solutions of methyl orange are given only when the concentration is less than 2×10^{-4} gram-molecules per liter. Considerable difficulty was encountered during the preliminary work, owing to the fact that the indicator solutions were more concentrated than the above-named limit. Such solutions of methyl orange, especially those containing a large excess of acid and also those with enough acid to give an intense red color, gradually become more transparent on standing. The action of light very greatly accelerates this bleaching process. The solutions most susceptible to the action of light and of time are those containing the greatest amounts of acid. It was found that these solutions could be kept in the dark for 4 or 5 hours unchanged, and that bleaching again took place as soon as they were exposed to the light. Experiments were made which showed that light of the shorter wavelengths was more actinic in increasing the transparency of the solutions

than light of longer wave-lengths. The addition of 10 per cent of ethyl alcohol rendered these solutions fairly stable to the action of light and time. After standing for a day or two, solutions containing an excess of acid often showed the presence of fine crystals. Large amounts of these crystals could be obtained by strongly acidifying a saturated solution of methyl orange. It is thought that the formation of these crystals, very probably helianthine itself, causes the instability of the solutions in question. The obvious procedure to follow was to use more dilute solutions, which were found to be quite stable, and even the solution containing the excess of acid would remain practically unchanged when exposed to the action of light for a short time. However, when the concentration of methyl orange approximated 2×10^{-4} gram-molecules per liter, as is the case for the solutions given in table 32, the solution containing an excess of acid was prepared last and its percentage transmission measured immediately. The remaining solutions were kept in the dark until used. It is certain that when such precautions are taken, no appreciable change in transparency could occur before the radiometric measurements were completed. Table 32, the concentration of the methyl orange being 1.98×10^{-4} gram-molecules per liter, indicates that even the solutions containing an excess of acid can be safely used in this way.

The following shows how accurately small concentrations of hydrogen and hydroxyl ions can be estimated by radiometric measurements. If the percentage transmission for the various solutions be plotted as curves, the abscissæ being wave-lengths and the ordinates percentage transmissions, it will be noted that with increasing amounts of acid the transmission curve for pure methyl orange is widely displaced towards the red end of the spectrum. The solution curve corresponding to the excess of acid is displaced about 400 Å. u. from the curve corresponding to a pure aqueous solution of methyl orange. From the displacements produced by solutions containing known amounts of acid, and the displacement given by a solution containing an unknown amount, the concentration of the unknown amount of acid can be quite accurately and quickly determined. In one case a solution was prepared containing an amount of sulphuric acid unknown to us. The concentration of the acid was determined by the above method, and the value found was 0.00000216 gram per cubic centimeter. The amount actually present was 0.00000210 gram per cubic centimeter. Several similar attempts were made and they were quite as successful.

RESULTS WITH METHYL ORANGE.

The hydrolysis and ionization constants for methyl orange, recorded in Tables 33 and 35, are to be regarded as part of the preliminary work. Table 32 contains the percentage transmissions for nine solutions of methyl orange prepared in accordance with the scheme given below. The concentration of the mother solutions of methyl orange was 3.973

$\times 10^{-4}$; that of the mother solution of sulphuric acid 3.0885×10^{-4} gram-molecules per liter.

SOLUTIONS.

- I. 50 c.c. methyl orange, diluted to 100 c.c.
- II. 50 c.c. methyl orange, 5 c.c. sulphuric acid, diluted to 100 c.c.
- III. 50 c.c. methyl orange, 10 c.c. sulphuric acid, diluted to 100 c.c.
- IV. 50 c.c. methyl orange, 15 c.c. sulphuric acid, diluted to 100 c.c.
- V. 50 c.c. methyl orange, 20 c.c. sulphuric acid, diluted to 100 c.c.
- VI. 50 c.c. methyl orange, 30.9 c.c. sulphuric acid, diluted to 100 c.c.
- VII. 50 c.c. methyl orange, 35 c.c. sulphuric acid, diluted to 100 c.c.
- VIII. 50 c.c. methyl orange, 1.0 c.c. conc. sulphuric acid, diluted to 100 c.c.
- IX. 50 c.c. methyl orange, 2.0 c.c. conc. sulphuric acid, diluted to 100 c.c.

TABLE 32.

[I/I₀ for depth of solution = 20 mm.]

$\lambda = \text{\AA. U.}$	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	Average of VIII and IX.
5748	84.6		71.9	65.1	57.7	49.1	46.7	9.5	8.4	8.95
5798	90.0	85.6	79.3	73.3	70.0	62.2	61.0	22.1	22.1	22.1
5847	91.4		84.6	81.4	77.9	70.3		35.7	35.7	35.7

Attention is called to the blank spaces appearing in some of the tables. For some solutions and certain wave-lengths of light no transmission values were obtained. It was known at the time the measurements were made that certain transmission values were erroneous, due either to variations in the current intensity or to vibrational disturbances. The action of light, as has been previously explained, renders these solutions of methyl orange more transparent, and for this reason it was necessary to complete the reading as soon as possible. This excluded the possibility of remeasuring the percentage transmissions made when conditions were unfavorable for accurate readings.

Table 33 gives the quinoid-salt and azo-base concentrations of each of the above solutions, the hydrolysis constant (K_w/K_i), and the ionization constant K_i of methyl orange as a base.

TABLE 33.

Solution.	$\lambda = \text{\AA. U.}$	Azo-base $c' \times 10^4$.	Quinoid salt. $c \times 10^5$.	$K_w/K_i \times 10^4$.	$K_i \times 10^{11}$.
II	5798	1.91	0.353	6.5	1.3
III	5748	1.84	0.716	6.1	1.3
	5797	1.80	0.897	4.4	1.8
	5847	1.82	0.813	5.1	1.6
IV	5748	1.75	1.16	5.2	1.6
	5797	1.69	1.46	3.7	2.2
	5847	1.74	1.23	4.8	1.7
V	5748	1.64	1.69	4.4	1.9
	5797	1.63	1.78	4.0	2.0
	5847	1.65	1.68	4.4	1.8
VI	5748	1.50	2.41	4.5	1.8
	5797	1.46	2.61	3.9	2.0
	5847	1.43	2.76	3.5	2.3
VII	5847	1.46	2.62	4.6	1.8
	5797	1.46	2.65	4.5	1.8
				Av., 4.5×10^{-4}	Av., 1.8×10^{-11}

The calculations of the hydrolysis and ionization constants are based on logarithmic functions; and where the transmission of the solution is nearly complete, a slight variation from the actual percentage transmission will cause a great change in the calculated hydrolysis and ionization constants. If we consider an experimental case where the amount of absorption to be measured is slight, the above can be made quite clear. Solution II in table 32 for wave-length of light $\lambda = 5798$ Å. U. actually gave a percentage transmission of 85.6. Changing the percentage transmission by small amounts, and calculating the value of the hydrolysis and ionization constants from these values, we have

I/I_0 .	K_w/K_i .	K_i .
85.6	6.46×10^{-4}	1.25×10^{-11} found experimentally
86.0	7.21×10^{-4}	1.12×10^{-11}
86.6	8.59×10^{-4}	0.94×10^{-11}

It will thus be seen that changing the percentage transmission by about 1 per cent will cause a variation in the ionization constant of about 25 per cent. When conditions are not satisfactory, it is quite possible that the error in some of the percentage transmissions may be greater than 1 per cent. Considering these facts, the constants show that the efforts which were made to eliminate errors arising from variations of the current intensity and vibrational disturbances were fairly successful.

The transmission values given in table 34 are for a much more dilute solution of methyl orange. The concentration of the mother solution of methyl orange was 1.9865×10^{-4} gram-molecules per liter; that of the mother solution of sulphuric acid being 3.0885×10^{-4} gram-molecules per liter.

SOLUTIONS.

- I. 50 c.c. methyl orange, diluted to 100 c.c.
- II. 50 c.c. methyl orange, 10 c.c. sulphuric acid, diluted to 100 c.c.
- III. 50 c.c. methyl orange, 15 c.c. sulphuric acid, diluted to 100 c.c.
- IV. 50 c.c. methyl orange, 20 c.c. sulphuric acid, diluted to 100 c.c.
- V. 50 c.c. methyl orange, 1 c.c. conc. sulphuric acid, diluted to 100 c.c.
- VI. 50 c.c. methyl orange, 0.5 c.c. conc. sulphuric acid, diluted to 100 c.c.
- VII. 50 c.c. methyl orange, 0.2 c.c. conc. sulphuric acid, diluted to 100 c.c.
- VIII. 50 c.c. methyl orange, 0.5 c.c. conc. sulphuric acid, diluted to 100 c.c.

TABLE 34.

[I/I_0 for depth of solution = 20 mm.]

$\lambda = \text{Å. U.}$	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	Average V, VI, VII and VIII.
5698	87.7	75.3	67.6	66.3	16.6	15.2	15.2	17.1	16.0
5723	88.9	80.7	74.2	72.3	20.1	20.1	20.2		20.1
5748	90.3	83.7	79.8	76.6	31.9	31.2	30.7	30.3	31.3
5773	91.6		81.7	81.3	38.8	39.0	39.5	41.1	39.9
5797	93.5	88.9	85.1	84.4	48.1	49.2	48.7	47.5	48.4
5823	94.5	91.3	87.0	86.2	55.3	53.8	55.0	56.4	55.1
5847	95.6	91.7		88.2	63.2	62.6	61.4	61.7	62.2

The constants given in table 35 are calculated from the values in table 34.

The ionization constants for methyl orange, recorded in tables 33 and 35, do not by any means represent the most accurate values that can be obtained by this radiometric method. It is necessary that the measurements be made in a region of the spectrum where the light energy is not intense, and, consequently, the deflections of the radiomicrometer are small. The largest deflection that could be obtained for wavelengths of light $\lambda = 0.58 \mu$ was 60 mm. It is for this reason that vibrations, and variations in the intensity of the Nernst glower, seriously interfere with the accuracy of the percentage transmissions. The temperature which prevailed at the time these measurements were made was not accurately known. However, it is certain that it was between 20° and 23° . The constants were calculated for 20° ; therefore, there is good reason to suppose that the real constants are somewhat higher (see table 37).

TABLE 35.

Solution.	$\lambda = \text{\AA. U.}$	Azo-base $c' \times 10^6$.	Quinoid salt. $c \times 10^6$.	$K_w/K_i \times 10^4$.	$K_i \times 10^{11}$.
IV	5698	8.30	8.14	5.5	1.5
	5723	8.55	6.88	6.8	1.2
	5748	8.41	7.62	6.0	1.4
	5773	8.49	7.18	6.4	1.3
	5797	8.42	7.56	6.0	1.4
	5823	8.22	8.56	5.1	1.6
III	5847	8.06	9.36	4.5	1.8
	5698	8.42	7.58	4.3	1.9
	5723	8.72	6.03	5.8	1.4
	5748	8.78	5.76	6.2	1.3
	5773	8.55	6.88	4.9	1.7
	5797	8.54	6.95	4.8	1.7
II	5823	8.40	7.63	4.3	1.9
	5698	9.04	4.47	5.3	1.5
	5723	9.28	3.24	7.9	1.0
	5748	9.22	3.53	7.1	1.1
	5797	9.20	3.62	6.9	1.2
	5823	9.28	3.22	8.0	1.0
	5847	8.96	4.84	4.8	1.7
				Av., 5.8×10^{-4}	Av., 1.5×10^{-11}

The transmission values given in table 36 were obtained when the temperature at the time of measurement was known to be 20° . The measurements were made at night, when the building was fairly free from vibrations. Under these conditions, the scale could be read accurately to 0.25 mm. Except for solutions II and VI, the current intensity remained very constant. A different mother solution of methyl orange was used, its concentration being 3.054×10^{-4} gram-molecules per liter. The concentration of the mother solution of sulphuric acid was 3.089×10^{-4} gram-molecules per liter.

SOLUTIONS.

- I. 50 c.c. methyl orange, diluted to 100 c.c.
 II. 50 c.c. methyl orange, 10 c.c. sulphuric acid, diluted to 100 c.c.
 III. 50 c.c. methyl orange, 15 c.c. sulphuric acid, diluted to 100 c.c.
 IV. 50 c.c. methyl orange, 20 c.c. sulphuric acid, diluted to 100 c.c.
 V. 50 c.c. methyl orange, 25 c.c. sulphuric acid, diluted to 100 c.c.
 VI. 50 c.c. methyl orange, 40 c.c. sulphuric acid, diluted to 100 c.c.
 VII. 50 c.c. methyl orange, 0.7 c.c. conc. sulphuric acid, diluted to 100 c.c.
 VIII. 50 c.c. methyl orange, 0.8 c.c. conc. sulphuric acid, diluted to 100 c.c.

TABLE 36.

[I/I₀ for depth of solution = 20 mm. Temperature = 20°.]

$\lambda = \text{\AA. U.}$	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	Average VII and VIII.
5723	88.2	71.8	63.7	58.0	51.6		11.8	11.6	11.7
5748	90.0	77.6	68.6	64.0	59.8		17.1	17.6	17.4
5773	91.6		75.2	71.0	67.4		24.8	24.9	24.9
5797	93.4		78.7	76.2	72.6	63.8	32.5	33.2	32.4
5848	95.4	89.6	86.6	84.5		75.2	49.0	49.8	49.4
5898	97.2		91.4	89.8	88.7		63.5	63.5	63.5

The values calculated from table 36 are recorded in table 37.

TABLE 37.

Solution.	$\lambda = \text{\AA. U.}$	Azo-base $c' \times 10^4$.	Quinoid salt $c \times 10^5$.	$K_w/K_4 \times 10^4$.	$K_4 \times 10^{11}$.
VI	5797	0.975	2.76	3.4	2.4
	5848	0.975	2.76	3.4	2.4
V	5723	1.193	1.67	4.3	1.9
	5748	1.147	1.99	3.5	2.3
	5773	1.167	1.80	3.8	2.1
	5797	1.203	1.62	4.5	1.8
	5898	1.197	1.65	4.4	1.8
IV	5723	1.211	1.58	3.5	2.3
	5748	1.211	1.58	3.5	2.3
	5773	1.227	1.50	3.8	2.1
	5798	1.235	1.46	4.0	2.0
	5848	1.315	1.36	4.7	1.8
III	5898	1.245	1.42	4.2	1.9
	5723	1.281	1.23	3.5	2.3
	5748	1.277	1.25	3.5	2.3
	5773	1.295	1.16	3.9	2.1
	5798	1.269	1.24	3.5	2.3
II	5848	1.309	1.09	4.3	1.9
	5898	1.301	1.13	4.0	2.0
	5723	1.372	0.773	4.1	2.0
	5748	1.390	0.687	4.9	1.7
	5848	1.383	0.718	4.6	1.8
				Av., 4.0×10^{-4}	Av., 2.1×10^{-11}

The greatest variation from the mean is less than 20 per cent. It has already been shown, in one experimental case, that an error of 1 per cent in the percentage transmission would cause a variation of 25 per cent in the ionization constant. The determination of the percentage transmissions from which the constants recorded in table 37 were cal-

culated, was made under the most favorable conditions. These constants, therefore, more likely represent the true constants of the indicator.

PHENOLPHTHALEIN.

Regarding phenolphthalein as a monobasic acid, we have from equation 2

$$\frac{\bar{Q} \times \overset{+}{H}}{LH} = K_i$$

Dividing this by the ion product of water, it follows that

$$\frac{LH \times \bar{OH}}{Q^+} = \frac{K_w}{K_i} \quad (21)$$

Phenolphthalein has but one component of absorption, and the application of Beer's law is much simpler than for methyl orange where there are two components of absorption. A solution of phenolphthalein in pure water is perfectly transparent. The addition of an excess of sodium hydroxide converts all the colorless lactoid molecules into the red quinoid salt, the concentration of which we will represent by c' . Let c be the concentration of the quinoid salt in the phenolphthalein solutions containing ammonium hydroxide and ammonium chloride. Since the depth of solution was maintained constant, we have the two fundamental equations given below:

$$\ln (I/I_0) = -Kc \quad (22)$$

$$\ln (I/I_0)' = -Kc' \quad (23)$$

The constant K is the same in both cases. Dividing 22 by 23 we have

$$\frac{\ln (I/I_0)}{\ln (I/I_0)'} = c/c' \text{ or } c = \frac{c' \times \ln (I/I_0)}{\ln (I/I_0)'} \quad (24)$$

Where $(I/I_0)'$ is the percentage transmission of a solution of phenolphthalein containing an excess of alkali, for some given wave-length of light; (I/I_0) that for the solution in which the concentration of the quinoid salt c , is to be determined for the same wave-length of light. Knowing, then, the amount of phenolphthalein converted into the quinoid salt, LH in equation 21 is given by $T - c$, where T represents the total amount of phenolphthalein. The hydroxyl ion concentration was varied by the addition of ammonium chloride to ammonium hydroxide.

The value of OH to be substituted in the hydrolysis equation for phenolphthalein was obtained from the following equation:

$$\frac{\overset{+}{NH_4} \times \bar{OH}}{(\overset{+}{NH_4}OH + NH_3)} = K_b$$

If ammonium chloride and ammonium hydroxide are present in the same solution, the concentration of the NH_4 ions is furnished almost entirely by the ammonium chloride. Let S equal the concentration of the salt and B the concentration of the base. We then have for dilute solutions

$$\frac{S \times \bar{\text{OH}}}{B} = K_b \quad (25)$$

or

$$\bar{\text{OH}} = \frac{K_b \times B}{S} \quad (26)$$

The ionization constant for ammonium hydroxide¹ at 25° is given as 18×10^{-6} . All of the work on phenolphthalein was done at 20°, and reducing the above value to 20°, we obtain from equation 20, q being equal to 1,400 calories, $K_b = 17.4 \times 10^{-6}$.

A pure sample of phenolphthalein was recrystallized from absolute methyl alcohol. A weighed amount of purified phenolphthalein was dissolved in 50 c.c. of absolute ethyl alcohol. By means of a small pipette, carefully calibrated, a small volume of this alcoholic solution, say 1.25 c.c., could be quite accurately measured. This volume was diluted with conductivity water to 2,000 c.c. Experiments were made which showed that the effect of this small trace of alcohol was negligible. (See McCoy.) The ammonia employed for the solution of ammonium hydroxide was distilled from barium hydroxide to eliminate carbon dioxide. All solutions were prepared with conductivity water at 20°. Special care was taken to prevent carbon dioxide from coming in contact with any of the solutions.

It is well known that an excess of alkali causes a rather rapid fading of solutions of phenolphthalein. Experiments were made which showed that a very slight error would be introduced if the solutions of phenolphthalein containing an excess of alkali were used directly after being prepared. Filling the cells with the solution, and taking radiometric measurements for 5 wave-lengths of light, required about 8 minutes, and during this short space of time the change in transparency was found to be very slight.

A few of the experiments made with solutions of phenolphthalein containing an excess of alkali are recorded in table 38. All solutions were diluted to 100 c.c. and each contained equal amounts of phenolphthalein. A normal solution of sodium hydroxide was used for these experiments. The percentage transmissions given by solutions I and II are for 0.8 c.c. and 1 c.c., respectively, of the alkali. The interval which elapsed between the time the solutions were prepared and the last measurement made was between 7 and 8 minutes. Measurements

¹Carnegie Inst. Wash. Pub. No. 63, 298 (1907).

were again made with solution II, 15 minutes later. The results are recorded under III. By comparing the transmission values, the effect of the bleaching for an interval of 15 minutes can be noted. Solution IV contained 0.5 c.c. alkali, and was kept in the dark nearly a half-hour before being used. Solution V, containing 1 c.c. of alkali, was used about 4 hours after being prepared.

Similar experiments were made with solutions of phenolphthalein, partially converted into the quinoid salt, and it was found that such solutions are fairly stable. Very little change in transparency could be detected during the first 4 or 5 hours after the solutions were prepared.

TABLE 38.
[I/I₀ for depth of solution = 20 mm.]

$\lambda = \text{\AA. U.}$	I.	II.	III.	IV.	V.
5773	10.5	10.1	12.1	10.1	24.9
5798	15.2	15.4	16.5	15.2	31.0
5823	20.8	20.2	22.6	21.4	37.8
5848	28.7	27.4	30.3	28.4	45.6
5947	59.4	57.7	61.2	60.3	71.1

RESULTS WITH PHENOLPHTHALEIN.

The six solutions recorded below were prepared from the following mother solutions. The concentration of the phenolphthalein was 6.697×10^{-5} gram-molecules per liter; that of the ammonium hydroxide 0.1448 gram-molecules per liter, and that of the ammonium chloride 0.1 gram-molecules per liter.

SOLUTIONS.

- I. 75 c.c. phenolphthalein, diluted to 100 c.c.
- II. 75 c.c. phenolphthalein, 2 c.c. NH_4OH , 1 c.c. NH_4Cl , diluted to 100 c.c.
- III. 75 c.c. phenolphthalein, 2 c.c. NH_4OH , 2 c.c. NH_4Cl , diluted to 100 c.c.
- IV. 75 c.c. phenolphthalein, 2 c.c. NH_4OH , 5 c.c. NH_4Cl , diluted to 100 c.c.
- V. 75 c.c. phenolphthalein, 2 c.c. NH_4OH , 10 c.c. NH_4Cl , diluted to 100 c.c.
- VI. 75 c.c. phenolphthalein, 1 c.c. N NaOH , diluted to 100 c.c.

TABLE 39.
[I/I₀ for depth of solution = 20 mm. Temperature = 20°.]

$\lambda = \text{\AA. U.}$	I.	II.	III.	IV. N	V.	VI.
5773	100.0	30.8	46.3	70.7		10.1
5798	100.0	37.8	53.4	76.3	86.7	14.3
5823	100.0	45.3	58.9	78.5	89.3	20.2
5848	100.0	51.7	66.2	83.0	91.3	27.4
5948	100.0		83.7			57.7

The percentage transmissions for these solutions are given in table 39. The concentrations of the two tautomeric forms, and the hydrolysis and ionization constants calculated from table 39 are recorded in table 40.

TABLE 40.

Solution.	$\lambda = \text{\AA. U.}$	Lactoid form $c \times 10^5$.	Quinoid salt $c \times 10^5$.	$\text{OH} \times 10^5$.	$K_{\text{H}}/K_{\text{t}} \times 10^5$.	$K_{\text{t}} \times 10^{10}$.	Average $K_{\text{t}} \times 10^{10}$.
II	5773	2.44	2.58	5.039	4.77	1.70	
	5798	2.51	2.51	5.039	5.05	1.60	1.63
	5823	2.54	2.48	5.039	5.17	1.57	
	5848	2.46	2.56	5.039	4.85	1.67	
III	5773	3.33	1.69	2.519	4.96	1.64	
	5798	3.40	1.62	2.519	5.27	1.54	
	5823	3.35	1.67	2.519	5.06	1.60	1.56
	5848	3.42	1.60	2.519	5.38	1.51	
	5948	3.40	1.62	2.519	5.28	1.53	
IV	5773	4.26	0.757	1.007	5.68	1.43	
	5798	4.32	0.696	1.007	6.27	1.20	1.38
	5823	4.26	0.761	1.007	5.63	1.44	
	5848	4.30	0.720	1.007	6.02	1.35	
V	5798	4.65	0.369	0.503	6.37	1.27	
	5823	4.67	0.356	0.503	6.63	1.22	1.23
	5848	4.67	0.352	0.503	6.68	1.21	

The series of solutions the results of which are recorded in table 41 were prepared from another solution of phenolphthalein. Its concentration was 4.603×10^{-5} gram-molecules per liter. The concentrations of the ammonium hydroxide and ammonium chloride solutions were the same as for the previous series. It will be noticed that 1 c.c. of a solution of ammonium hydroxide was used instead of 2 c.c. as in the former case.

SOLUTIONS.

- I. 75 c.c. phenolphthalein, 1 c.c. NH_4OH , 0.5 c.c. NH_4Cl , diluted to 100 c.c.
- II. 75 c.c. phenolphthalein, 1 c.c. NH_4OH , 1 c.c. NH_4Cl , diluted to 100 c.c.
- III. 75 c.c. phenolphthalein, 1 c.c. HN_4OH , 2 c.c. NH_4Cl , diluted to 100 c.c.
- IV. 75 c.c. phenolphthalein, 1 c.c. NH_4OH , 2.5 c.c. NH_4Cl , diluted to 100 c.c.
- V. 75 c.c. phenolphthalein, 0.8 c.c. N NaOH , diluted to 100 c.c.

TABLE 41.

[I/I_0 for depth of solution = 20 mm. Temperature = 20° .]

$\lambda = \text{\AA. U.}$	I.	II.	III.	IV.	V.
5773	48.2	62.2	73.0	81.3	15.7
5798	54.2	66.3	78.7	83.0	22.7
5823	59.6	70.7	83.9	86.0	30.5
5848	66.4	74.6	85.1	89.0	37.9
5948	84.8	87.7		94.8	62.2

TABLE 42.

Solution.	$\lambda = \text{\AA. U.}$	Lactoid form $c \times 10^5$.	Quinoid salt $c \times 10^5$.	$\text{OH} \times 10^5$.	K_u/K_t $\times 10^5$.	$K_t \times 10^{10}$.	Average $K_t \times 10^{10}$.
I	5773	2.09	1.36	5.039	7.79	1.04	
	5798	2.03	1.42	5.039	7.24	1.12	1.14
	5823	1.95	1.50	5.039	6.56	1.23	
	5848	1.99	1.46	5.039	6.92	1.17	
II	5773	2.56	0.884	2.519	7.31	1.11	
	5798	2.49	0.953	2.519	6.61	1.23	
	5823	2.44	1.006	2.519	6.13	1.32	1.25
	5848	2.41	1.040	2.519	5.83	1.39	
III	5948	2.49	0.951	2.519	6.61	1.23	
	5773	2.86	0.587	1.259	6.15	1.32	
	5798	2.89	0.557	1.259	6.53	1.24	1.21
	5823	2.94	0.508	1.259	7.96	1.02	
IV	5848	2.87	0.573	1.259	6.37	1.27	
	5773	3.05	0.386	1.007	8.03	1.01	
	5798	3.01	0.433	1.007	7.01	1.15	
	5823	3.01	0.436	1.007	7.01	1.15	1.06
	5848	3.03	0.413	1.007	7.42	1.09	
	5948	3.06	0.385	1.007	8.04	1.01	

The concentrations of the mother solutions used in the preparation of the solutions for the following series of measurements were the same as those employed for table 39. The results are recorded in tables 43 and 44.

SOLUTIONS.

- I. 75 c.c. phenolphthalein, 0.5 c.c. NH_4OH , 0.5 c.c. NH_4Cl , diluted to 100 c.c.
 II. 75 c.c. phenolphthalein, 0.5 c.c. NH_4OH , 1 c.c. NH_4Cl , diluted to 100 c.c.
 III. 75 c.c. phenolphthalein, 0.5 c.c. NH_4OH , 2 c.c. NH_4Cl , diluted to 100 c.c.
 IV. 75 c.c. phenolphthalein, 0.8 c.c. N NaOH , diluted to 100 c.c.

TABLE 43.

$[I/I_0 \text{ for depth of solution} = 20 \text{ mm. Temperature} = 20^\circ.]$

$\lambda = \text{\AA. U.}$	I.	II.	III.	IV.
5773	63.2	76.2	87.3	9.9
5798	65.8	80.3	89.2	14.7
5823	72.0	82.8	91.5	20.4
5848	74.3			27.4
5948	88.8	93.3		57.6

TABLE 44.

Solution.	$\lambda = \text{\AA. U.}$	Lactoid form $c \times 10^5$.	Quinoid salt $\times 10^5$.	$\text{OH} \times 10^5$.	K_u/K_t $\times 10^5$.	$K_t \times 10^{10}$.	Average $K_t \times 10^{10}$.
I	5773	4.026	0.99	2.519	10.16	0.80	
	5798	3.935	1.09	2.519	9.07	0.99	
	5823	3.985	1.04	2.519	9.65	0.83	0.89
	5848	3.875	1.15	2.519	8.47	0.97	
II	5948	3.955	1.07	2.519	9.28	0.87	
	5773	4.43	0.59	1.26	9.46	0.86	
	5798	4.45	0.57	1.26	9.77	0.83	0.87
	5823	4.42	0.60	1.26	9.24	0.88	
III	5948	4.39	0.62	1.26	8.82	0.92	
	5773	4.73	0.30	0.63	10.07	0.81	
	5798	4.73	0.30	0.63	10.00	0.81	0.79
	5823	4.74	0.28	0.63	10.65	0.75	

The concentration of phenolphthalein is not a factor in the variations of the constants in the different tables. The following shows that it is possible to determine K_i without knowing the concentration of the indicator.

If we consider equation 21

$$\frac{\text{LH} \times \bar{\text{OH}}}{\text{Q}^+} = \frac{K_w}{K_i}$$

and represent the total concentration of phenolphthalein by T , and that of the quinoid salt by Q , we have from equation 24

$$\frac{\ln (I/I_0) \times T}{\ln (I/I_0)'} = Q$$

LH is then equal to $(T - Q)$ or

$$\text{LH} = (T - Q) = T - \frac{\ln (I/I_0) \times T}{\ln (I/I_0)'} \quad (27)$$

Substituting these values in the hydrolysis equation, we have

$$\frac{\left[T - \frac{\ln (I/I_0) \times T}{\ln (I/I_0)'} \right] \times \bar{\text{OH}}}{\frac{\ln (I/I_0) \times T}{\ln (I/I_0)'}} = \frac{K_w}{K_i} \quad (28)$$

Simplifying, T , the concentration of the phenolphthalein disappears, and we have

$$\frac{\bar{\text{OH}}[\ln (I/I_0)' - \ln (I/I_0)]}{\ln (I/I_0)} = \frac{K_w}{K_i} \quad (29)$$

K_i , calculated from equation 29, gives the same value as when calculated from the equations previously derived.

Since it is not necessary to know the concentration of the indicator to determine its ionization constant, the variation of K_i , shown by the different tables, must be due to other causes. It will be noticed from the separate tables that K_i decreases with the hydroxyl ion concentration. This is in accordance with the results of previous investigators. When the hydroxyl ion concentration, or the ratio of ammonium chloride to ammonium hydroxide remains the same, K_i shows a marked decrease with decreasing amounts of neutral salts. If we consider solutions III and I in tables 40 and 44, respectively, it will be seen that decreasing the concentration of the neutral salt four times changes K_i from 1.6×10^{-10} to 0.9×10^{-10} . This is in accord with the results of Rosenstein, who has made a very careful study of the effect of neutral salts on the ionization constant of phenolphthalein. It will, therefore, be seen that the discrepancies in the value of K_i are due in part at least

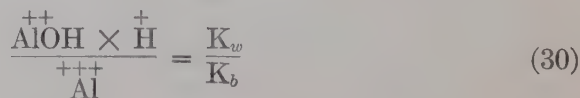
to the effect of the neutral salt. From this it might be concluded that K_i would be largest for those solutions containing the greatest amount of neutral salt. A study of the separate tables, table 40 for instance, shows that just the reverse is true. The solution that contains the largest amount of neutral salt always gives the smallest concentration of hydroxyl ions, and the K_i value for such a solution is much lower than for a solution containing less neutral salt but a greater concentration of hydroxyl ions. It is thus evident that K_i varies not only with the concentration of the neutral salt, but also with the concentration of the hydroxyl ions. From the above it will be seen that if the neutral salt had no effect, the variation of K_i in the separate tables would be much greater than it actually is. It is therefore obvious that the equilibrium equations, based on the assumption that phenolphthalein acts as a monobasic acid, do not hold.

Wegscheider concludes that these variations may be accounted for by regarding phenolphthalein as a dibasic acid. The results of Rosenstein make it appear very probable that this indicator does act as a dibasic acid. The limitations of this method and the presence of neutral salts made it impossible for him to determine satisfactorily the ionization constant for phenolphthalein, and the question must therefore be regarded as still open.

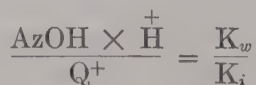
The radiometric method has thus far been applied for determining the hydrolysis and ionization constants of indicators. Knowing these values, it is possible, by radiometric means, to determine from them the hydrolysis constants of many salts. The calculation of the ionization constants of weak acids and bases formed by the hydrolysis of these salts is then a simple matter.

This method has been applied in a preliminary way to aluminum sulphate, using methyl orange as the indicator. It is assumed that the secondary and tertiary hydrolysis of this salt can be neglected, and, on this assumption, the ionization constant of the base formed by the primary hydrolysis has been calculated.

The calculations of the constants are based on two fundamental equilibrium equations, the symbols representing gram-ions per liter. Expressing the equilibrium relation for the primary hydrolysis of aluminum sulphate, we have



In the hydrolysis equation for methyl orange,



K_i has been determined and K_w is known. The concentration of the quinoid ions $\overset{+}{Q}$ is given by

$$\overset{+}{Q} = \frac{T[\ln(I/I_0) - \ln(I/I_0)']}{\ln(I/I_0)'' - \ln(I/I_0)'} \quad (31)$$

as explained in equation 19. If the total amount of indicator is T , $AzOH = T - \overset{+}{Q}$. We then have all the data necessary for the calculation of the hydrogen ion concentration in equation 30. The concentration of the ion $\overset{+}{AlOH}$ in the same equation is given by $\overset{+}{H} + \overset{+}{Q}$, both of which have been determined. If T' represents the total salt added and α its dissociation, Al is $(T' - \overset{+}{AlOH}) \alpha$.

The following solutions were prepared from mother solutions of methyl orange and aluminium sulphate, the concentrations being 1.9865×10^{-4} and 0.391 gram-molecules per liter, respectively.

SOLUTIONS.

- I. 50 c.c. methyl orange, diluted to 100 c.c.
- II. 50 c.c. methyl orange, 5 c.c. $Al_2(SO_4)_3$, diluted to 100 c.c.
- III. 50 c.c. methyl orange, 7 c.c. $Al_2(SO_4)_3$, diluted to 100 c.c.
- IV. 50 c.c. methyl orange, 10 c.c. $Al_2(SO_4)_3$, diluted to 100 c.c.
- V. 50 c.c. methyl orange, 0.5 c.c. conc. H_2SO_4 , diluted to 100 c.c.

The percentage transmissions given by these solutions are recorded in table 45.

TABLE 45.

$[I/I_0 \text{ for depth of solution} = 20 \text{ mm.}]$

$\lambda = \overset{\circ}{A. U.}$	I.	II.	III.	IV.	V.
5698	87.7	47.7	44.7	39.7	16.0
5723	88.9	56.7	53.1		20.1
5748	90.3	63.0	59.1	56.7	31.0
5773	91.6	70.2	66.8	63.6	39.9
5797	93.3	74.7	73.6	68.6	48.4
5823	94.5	78.4	78.1	75.5	55.1
5847	95.6	81.6		78.5	62.2

The constants calculated from these percentage transmissions are given in table 46. It has been found¹ that the dissociation of the aluminium sulphate in solutions II, III, and IV is approximately 35, 32, and 30 per cent, respectively.

¹Carnegie Inst. Wash. Pub. No. 170, 60 (1912).

TABLE 46.—Constants.

Solution.	$\lambda = \text{\AA. U.}$	$\frac{+}{Q}$ $10^6.$	Average AzOH $10^6.$	Average $\frac{+}{H}$ $10^4.$	Average $\frac{++}{AlOH}$ $10^4.$	Average $\frac{+++}{Al}$ $10^3.$	Average $K_w K_b$ $\times 10^6.$	Average $K_b \times 10^9.$
II	5698	3.56						
	5723	3.01						
	5748	3.35						
	5773	3.20	6.56	1.97	2.307	6.76	6.75	1.2
	5797	3.37						
	5823	3.44						
	5847	3.65						
III	5698	3.94						
	5723	3.44						
	5748	3.94	6.24	2.24	2.609	8.66	6.75	1.2
	5773	3.79						
	5797	3.50						
	5823	3.51						
	5847	4.62						
IV	5698	4.33						
	5748	4.36	5.49	3.12	3.564	11.62	9.70	0.84
	5773	4.66						
	5797	4.16						
	5823	4.16						
	5847	4.54						
								

SUMMARY.

A satisfactory radiomicrometer, having a half-period of 10 seconds and a sensibility of 5 per square millimeter of exposed vane (candle and scale being at a meter's distance) was constructed. Making use of the radiomicrometer and the grating spectroscope, a radiometric method was worked out for the determination of the ionization constants of indicators. This method is freer from objections and limitations than any method previously used. It serves as well for a two-colored indicator as for a one-colored indicator.

Very small concentrations of colored components were determined, and it has been shown that minute concentrations of hydrogen and hydroxyl ions can be quickly and accurately estimated by means of radiometric measurements.

Satisfactory constants were obtained for the ionization of methyl orange as a base. The value found is 2.1×10^{-11} .

The ionization and hydrolysis constants for phenolphthalein considered as a monobasic acid are far from being satisfactory.

From the known ionization constant of methyl orange and from radiometric measurements, the ionization constant of a very weak base and the hydrolysis constant of one of its salts have been roughly determined. The method can likewise be applied to the determination of the ionization constants of very weak acids, and the hydrolysis constants of the salts formed by these acids. Work is now in progress in this laboratory on other indicators from this same standpoint.

CHAPTER IV.

RADIOMETRIC MEASUREMENTS OF THE IONIZATION CONSTANTS OF INDICATORS.—II.

BY M. G. PAULUS AND J. F. HUTCHINSON.

An investigation of the ionization constants of methyl orange and phenolphthalein has already been published by Shaeffer, Paulus, and Jones.¹ A new method, based upon the absorption of light by solutions of indicators, was developed for the determination of the constants of indicators, and is now presented. It was shown that this method serves as well for a two-colored as for a one-colored indicator. The work recorded herein is to be regarded as a continuation of the original investigation, and the purpose is to test the applicability of the method to the determination of the ionization constant of rosolic acid. A description of the apparatus used has already been given in detail in the original paper.

THEORETICAL DISCUSSION.

Considering first of all that rosolic acid is monobasic,² the ionization constant K_i is expressed by the simple equilibrium equation

$$\frac{(H^+) \times (\overline{In})}{(HIn)} = K_i \quad (1)$$

If, then, the hydrogen ion concentration of the indicator solution is fixed, the ratio $(\overline{In})/(HIn)$ at equilibrium can be determined. It has been shown that the percentage transmission of a solution, such as that of rosolic acid, containing two absorbing components is given by the equation

$$\ln (I/I_0) = -Kc - K'c_1 \quad (2)$$

where c and c_1 are the concentrations of the two absorbing components, and K and K' are constants depending upon the nature of the absorbing components and the wave-length of light employed. Applying this equation to rosolic acid, let c represent the concentration of the red component, or $(\overline{In})$ in equation 1, and let c_1 represent the concentration of the yellow component or (HIn) . Equation 2, then, will represent the percentage transmission for some given depth of an incompletely transformed solution of rosolic acid. In a solution containing a large excess of acid $c=0$, and equation 2 becomes

$$\ln (I/I_0)' = -K'c_1 = -K'T \quad (3)$$

¹Journ. Amer. Chem. Soc., **37**, 776 (1915).

²The behavior of rosolic acid as a dibasic acid will be discussed later.

If a large excess of alkali¹ is added to the indicator solution $c_1=0$, and equation 2 reduces to

$$\ln (I/I_0)'' = -Kc = -KT \quad (4)$$

where T equals the total concentration of the indicator in solution. If the percentage transmissions are determined for the same depth of solution and for the same wave-length of light, and if the total concentration of the indicator is the same in all solutions, then the values of the constants K and K' given by equations 3 and 4 can be substituted in equation 2, whence

$$T \times \ln (I/I_0) = \ln (I/I_0)'' \times c + \ln (I/I_0)' \times c_1 \quad (5)$$

Since the total concentration of the indicator T is always equal to the sum of the two components, $T = c + c_1$, equation 5 reduces to

$$c/c_1 = \frac{\ln (I/I_0)' - \ln (I/I_0)}{\ln (I/I_0) - \ln (I/I_0)''} \quad (6)$$

The ratio $c/c_1 = (\bar{I}n)/HIn$ can be determined from equation 6. (I/I_0) is the percentage transmission for some given depth of the incompletely transformed solution under investigation, for some wave-length of light; $(I/I_0)'$ the percentage transmission of the indicator solution completely transformed into the yellow component for the same wave-length; and $(I/I_0)''$ the percentage transmission for the same depth of indicator solution completely transformed into the red component, for the same wave-length of light. The total concentration of the indicator in these three solutions must, of course, be the same, but the total concentration need not be known.

Returning now to equation 1, the method of obtaining all the data necessary for calculating the ionization constant is known, except that for determining the concentration of the hydrogen ion. This was fixed by solutions of disodium phosphate containing varying amounts of hydrochloric acid. The addition of hydrochloric acid converts the hydrophosphate ion almost quantitatively into the dihydrophosphate ion. The hydrogen ion concentration is given in such a solution by²

$$H^+ = \frac{1.95 \times 10^{-7} (H_2\bar{P}O_4)}{(H\bar{P}O_4)} \quad (7)$$

If we represent by a the concentration of the added hydrochloric acid, and by b the concentration of the disodium phosphate, then equation 7 becomes

$$H^+ = \frac{1.95 \times 10^{-7} \times a \alpha_1}{(b - a) \alpha_2} \quad (8)$$

where α_1 and α_2 represent respectively the dissociations of the mono- and disodium phosphates present at equilibrium.

¹By "a large excess" is meant sufficient alkali to convert the indicator entirely into its red component.

²The value of the constant was taken from the work of Abbott and Bray: Journ. Amer. Chem. Soc., **31**, 760 (1909).

If the quantity of disodium phosphate in the solutions investigated is always kept the same, the hydrogen ion concentration can be varied simply by the addition of different amounts of hydrochloric acid. In this case the total salt concentration is constant. This is extremely desirable, as it has been shown by Rosenstein¹ that neutral salts have a great effect upon the fraction of the indicator transformed. The value of the ionization constant in the case of phenolphthalein is doubled by increasing the total salt concentration from 0.03 to 0.40 normal.

PRELIMINARY WORK ON ROSOLIC ACID.

Three stock solutions were prepared, all solutions being made up at 20° with conductivity water. The stock solution of disodium phosphate was prepared from a pure sample obtained from Kahlbaum. Its concentration, 0.1036 gram-molecules per liter, was determined gravimetrically as magnesium pyrophosphate. The concentration of the stock solution of hydrochloric acid was 0.08085 normal. The stock indicator solution was prepared by dissolving about 0.4 gm. of an excellent sample of rosolic acid obtained from Merck in 2 liters of conductivity water. The total quantity of the indicator did not dissolve, but, as has been shown, it is not necessary to know the concentration of the indicator employed.

The incompletely transformed solutions to be tested were prepared from the stock solutions, so that all contained the same amounts of indicator and disodium phosphate, but different amounts of hydrochloric acid. This procedure was followed to keep the total salt concentration the same in all solutions. The volume of each solution was 100 c.c. The percentage transmissions (I/I_0), were taken with a 20 mm. depth of each solution, and for the same 5 wave-lengths of light. As explained in the original article, the percentage transmissions were determined by a differential method, which avoided the necessity of introducing certain correction factors due to the glass ends with which the cells were provided.

A consideration of equation 6 will show that the method of calculating the ratio of the red to the yellow component of any incompletely transformed indicator solution, not only depends upon the transmission of the solution under investigation, but also upon the transmission of an indicator solution containing a large excess of acid, in which the indicator is totally transformed into its yellow constituent; and also upon the transmission of an indicator solution having a large excess of alkali in which the indicator is totally transformed into its red component. Table 47 gives the results of a series of measurements made upon the indicator solution which has an excess of alkali. All solutions contain 50 c.c. of the stock solution of rosolic acid plus the

¹Abbott and Bray: Journ. Amer. Chem. Soc., **34**, 1128 (1912). See also: *Ibid.*, **37**, 804 (1915).

amount of N/1 NaOH indicated in the table, the solutions being in all cases diluted to 100 c.c. The percentage transmissions are given for 5 wave-lengths of light between $\lambda = 0.56\mu$ and $\lambda = 0.58\mu$, which is the region of the spectrum employed throughout this investigation. In certain cases the results of duplicate measurements are given, which indicate in a general way the accuracy of the results.

TABLE 47.
[I/I₀—depth of solution = 20 mm.]

$\lambda = \text{\AA. U.}$	0.5 c.c. N/1NaOH.	0.5 c.c. N/1NaOH after—								3.0 c.c. N/1NaOH after 24 hrs.	
		5 min.	10 min.	20 min.	30 min.	55 min.	5 hrs.		24 hrs.		
5598	22.6	16.1	12.5	10.7	9.08	7.55	6.25	6.37	6.53	6.53	9.16
5648	36.1	30.6	27.4	22.6	20.0	20.0	17.0	16.7	17.6	16.7	19.1
5698	52.3	44.8	44.2	38.8	37.9	37.0	34.5	34.5	32.2	32.2	35.6
5748	64.8	60.6	58.3	55.6	52.8	51.4	52.4	50.7	49.3	48.7	50.7
5798	77.0	73.3	71.1	68.4	64.1	64.8	66.6	66.2	63.5	63.7	66.3

Column 2, table 47, gives the percentage transmissions of an indicator solution containing 0.5 c.c. N/1 NaOH, the transmissions being determined within a short time after the solution was prepared. Columns 3 to 7, inclusive, give the percentage transmissions after the same solution had stood for various intervals of time up to 55 minutes. Columns 8 and 9 give the percentage transmissions of new indicator solutions containing the same amount of indicator and alkali, after these solutions had stood for 5 and 24 hours respectively. It will be observed that the percentage transmissions for any given wave-length of light become constant after the solutions have stood between 1 and 5 hours.

The fact that solutions of rosolic acid containing an excess of alkali become, on standing, less and less transparent to yellow light, clearly indicates that the concentration of the red component (In^-) present is becoming greater and greater, with a resulting decrease in the concentration of the yellow component (HIn); since the greater the concentration of the red component the more opaque the solution becomes to yellow light.

According to the most recent views¹ concerning the cause of color production by indicators of the aurine type, the color is not due simply to the presence of a quinoid group as such, but to an inter- or intramolecular combination of the metallic phenolate with the quinoid complex. It is very probably true, in the case of rosolic acid, that this combination between the metallic phenolate and the quinoid complex takes place rather slowly, with a corresponding intensification of the red color.

It will be observed that the transmission values recorded in column 10, table 47, of an indicator solution containing 3 c.c. N/1NaOH are

¹Amer. Chem. Journ., **39**, 537, 650, and 651 (1908).

considerably higher than those recorded in columns 8 and 9, for a solution containing 0.5 c.c. N/1NaOH. In both cases the solutions have come to equilibrium, since it has been shown that equilibrium is established after the solutions have stood between 1 and 5 hours. When very much larger amounts of alkali are added (say 10 c.c.), a very perceptible bleaching takes place. In solutions, then, containing an excess of sodium hydroxide, two opposing reactions take place; first, a gradual intensification of the red color brought about very probably by a time reaction between the metallic phenolate and the quinoid complex; and second, a bleaching of the red color which is greater the larger the amount of the alkali added. Since it is necessary to know the true percentage transmission $(I/I_0)''$ of a solution completely transformed into the red component, in order to determine the ratio c/c_1 , it follows that the bleaching must be avoided. This result can be obtained by keeping the concentration of the alkali as small as possible, only adding sufficient to transform completely the indicator. The obvious method was to increase gradually the hydroxyl ion concentration until the solutions were shown to be completely transformed. Table 48 gives the results of such a determination. All solutions contain 50 c.c. of the stock solution of indicator plus the amount of disodium phosphate and hydrochloric acid indicated in the table. All solutions were allowed to stand a sufficient length of time for equilibrium to be established.

TABLE 48.
 $[(I/I_0)'' - \text{depth of solution} = 20 \text{ mm.}]$

$\lambda = \text{\AA. U.}$	25 c.c. Na_2HPO_4 1 c.c. HCl. After 24 hrs.		25 c.c. Na_2HPO_4 0.5 c.c. HCl. After 48 hrs.	25 c.c. Na_2HPO_4 0 c.c. HCl. After 48 hrs.		25 c.c. Na_2HPO_4 0 c.c. HCl. After 96 hrs.
5598	4.44	4.35	4.68	4.68	4.76	5.00
5648	13.7	14.0	11.1	10.8	11.0	9.6
5698	22.8	22.8	19.4	19.4	18.8	19.0
5748	40.0	40.0	33.3	34.1	34.9	34.5
5798	51.6	51.0	48.4	48.4	49.4	48.8

Solution 1, table 48, in which the hydrogen ion concentration is 0.8266×10^{-8} , gives higher values for the percentage transmissions than solutions 2 and 3, in which the hydrogen ion concentrations are, respectively, 0.4157×10^{-8} and 0.043×10^{-8} . This shows that solution 1 is not completely transformed, since an increase in the red component and a corresponding decrease in the yellow component make the solution more opaque to yellow light. Solution 2 must, however, be completely transformed, since, when the hydrogen ion concentration is still further decreased, as is the case in solution 3, the transmission values remain the same. The values of the percentage transmissions recorded in columns 2, 3, and 4 are the values to be substituted for $(I/I_0)''$ in equation 6.

In order to ascertain if this same decrease in the transmissions, corresponding to an increase in the red component, would take place on standing with solutions of indicators which are incompletely transformed, the following series of solutions were prepared:

SOLUTIONS.

- No. 1. 50 c.c. rosolic acid; 25 c.c. Na_2HPO_4 ; 1 c.c. HCl diluted to 100 c.c.
 No. 2. 50 c.c. rosolic acid; 25 c.c. Na_2HPO_4 ; 5 c.c. HCl diluted to 100 c.c.
 No. 3. 50 c.c. rosolic acid; 25 c.c. Na_2HPO_4 ; 10 c.c. HCl diluted to 100 c.c.
 No. 4. 50 c.c. rosolic acid; 25 c.c. Na_2HOP_4 ; 15 c.c. HCl diluted to 100 c.c.

TABLE 49.

$[(I/I_0) - \text{depth of solution} = 20 \text{ mm.}]$

Solution.	$\lambda = \text{\AA. U.}$	After 5 hrs.		After 16 hrs.		After 24 hrs.	
1	5598	16.7	16.3			4.44	4.35
	5648	32.7	30.2			13.7	14.0
	5698	42.8	43.2			22.8	22.8
	5748	59.1	57.4			40.0	40.0
	5798	69.7	70.3			51.6	51.6
2	5598	30.8	30.8	25.7	25.0	26.4	26.4
	5648	39.3	39.6	35.4	35.9	37.5	35.7
	5698	52.6	51.7	48.3	40.0	50.0	49.3
	5748	66.1	64.5	60.8	60.7	60.3	59.4
	5798	72.7	74.3	71.0	71.0	70.7	70.6
3	5598	49.0	49.0	50.7	50.7	49.0	49.1
	5648	57.8	57.8	60.0	59.3	60.0	58.8
	5698	66.7	68.3	68.7	68.7	70.6	70.6
	5748	73.8	73.4	78.5	77.7	76.2	77.4
	5798	83.3	83.6	84.2	84.2	84.4	83.0
4	5598	66.1	67.3	68.0	67.2	67.3	67.8
	5648	72.4	74.1	74.9	74.3	76.4	76.4
	5698	81.6	80.3	81.3	80.4	81.0	79.5
	5748	83.2	83.2	87.2	87.2	85.5	85.5
	5798	88.2	89.4	90.2	90.2	87.7	87.8

In table 49 are given the percentage transmissions for a depth equal to 20 mm. of the above series of solutions. The transmissions were determined after the solutions had stood for intervals of 5, 16, and 24 hours. The transmission values recorded in columns 1 and 3 were determined with the same series of solutions. A new series of solutions was prepared for the 16-hour determination, the results of which are recorded in column 2. Solution No. 1 was not made up for this determination. Duplicate measurements are given in every case.

An examination of the transmission values recorded for solutions 1 and 2, table 49, shows that a decrease in the transmissions of incompletely transformed solutions of rosolic acid also takes place on standing. Solution 2, in which the hydrogen ion concentration is 4.484×10^{-8} , has come to equilibrium between 5 and 16 hours, as is shown by the fact that the transmission values become constant after 16 hours. In solutions 3 and 4, in which the hydrogen ion concentrations are respectively 10.53×10^{-8} and 19.52×10^{-8} , equilibrium was established before standing 5 hours. This points to the conclusion that in the incompletely transformed solutions of the indicator the more alkaline the solution the greater the time before equilibrium is established.

RESULTS WITH ROSOLIC ACID.

For the first determination of the indicator constant K_i the following series of solutions was used:

SOLUTIONS.

No. 1. 50 c.c. rosolic acid; 25 c.c. Na_2HPO_4 ; 5 c.c. HCl , diluted to 100 c.c.

No. 2. 50 c.c. rosolic acid; 25 c.c. Na_2HPO_4 ; 10 c.c. HCl , diluted to 100 c.c.

No. 3. 50 c.c. rosolic acid; 25 c.c. Na_2HPO_4 ; 15 c.c. HCl , diluted to 100 c.c.

These solutions were prepared from the stock solutions, the concentrations of which have already been given. All solutions were allowed to stand for 24 hours, which time, according to the results of the preliminary work, was amply sufficient for equilibrium to be established. In table 50 are given the percentage transmissions for a depth equal to 20 mm. of each of these solutions, the values being in every case the average of two measurements. These are the values to be substituted for (I/I_0) in equation 6. As has previously been explained, the ratio c/c_1 also depends upon the percentage transmission $(I/I_0)''$ of an indicator solution completely transformed into the red component, and also upon the percentage transmission $(I/I_0)'$ of an indicator solution completely transformed into the yellow constituent. The transmissions $(I/I_0)''$ used are the averages of those recorded in columns 2, 3, and 4, table 48. It was found that solutions containing 50 c.c. of the stock solution of the indicator plus the necessary amount of hydrochloric acid to convert the indicator entirely into the yellow component were completely transparent to the 5 wave-lengths of light used. The transmissions $(I/I_0)'$ are therefore in every case 100 per cent.

TABLE 50.

$\lambda = \text{\AA. U.}$	First solution. $\text{H}^+ \times 10^8 = 4.484.$			Second solution. $\text{H}^+ \times 10^8 = 10.53.$			Third solution. $\text{H}^+ \times 10^8 = 19.52.$		
	Average percentage transmissions	c/c_1	$K_i \times 10^8.$	Average percentage transmissions	c/c_1	$K_i \times 10^8.$	Average percentage transmissions	c/c_1	$K_i \times 10^8.$
5598	26.4	0.803	3.60	49.0	0.306	3.23	67.5	0.148	2.89
5648	36.6	0.811	3.64	59.4	0.302	3.19	76.4	0.136	2.66
5698	49.6	0.734	3.29	70.6	0.266	2.81	80.2	0.154	3.05
5748	59.8	0.920	4.13	76.8	0.326	3.44	85.5	0.171	3.34
5798	70.6	0.937	4.20	83.7	0.329	3.48	87.7	(0.223)	(4.35)

In table 50 the ratios $c/c_1 = (\overline{\text{In}})/(\text{HIn})$ were calculated from equation 6 and the constants K_i from equation 1. The hydrogen ion concentrations were calculated by means of equation 7, α_1 and α_2 being interpolated from the percentage ionizations of monosodium and disodium phosphates at various dilutions given by Abbott and Bray.¹

Another series of solutions described below was prepared and allowed to stand 16 hours, in which time all of them had come to

¹Amer. Chem. Journ., **31**, 729 (1909).

equilibrium. The percentage transmissions,¹ calculated ratios c/c_1 , and the constants K_i , are given in table 51. The same values for $(I/I_0)'$ and $(I/I_0)''$ were used as for the preceding determination.

SOLUTIONS.

- No. 1. 50 c.c. rosolic acid; 25 c.c. Na_2HPO_4 ; 3 c.c. HCl , diluted to 100 c.c.
 No. 2. 50 c.c. rosolic acid; 25 c.c. Na_2HPO_4 ; 5 c.c. HCl , diluted to 100 c.c.
 No. 3. 50 c.c. rosolic acid; 25 c.c. Na_2HPO_4 ; 10 c.c. HCl , diluted to 100 c.c.
 No. 4. 50 c.c. rosolic acid; 25 c.c. Na_2HPO_4 ; 15 c.c. HCl , diluted to 100 c.c.

TABLE 51.

$\lambda = \text{\AA. U.}$	First solution. $\text{H}^+ \times 10^8 = 2.533.$			Second solution. $\text{H}^+ \times 10^8 = 4.484.$		
	Average percentage transmissions.	c/c_1	$K_i \times 10^8$.	Average percentage transmissions.	c/c_1	$K_i \times 10^8$.
5598	12.1	2.28	5.77	25.4	0.822	3.69
5648	20.8	2.33	5.89	35.7	0.847	3.81
5698	32.0	2.20	5.56	48.3	0.785	3.53
5748	48.1	2.14	5.42	60.8	0.849	3.82
5798	60.9	2.22	5.63	71.0	0.906	4.07
$\lambda = \text{\AA. U.}$	Third solution. $\text{H}^+ \times 10^8 = 10.53.$			Fourth solution. $\text{H}^+ \times 10^8 = 19.52.$		
	Average percentage transmissions.	c/c_1	$K_i \times 10^8$.	Average percentage transmissions.	c/c_1	$K_i \times 10^8$.
5598	50.7	0.288	3.03	67.6	0.148	2.89
5648	59.7	0.298	3.14	74.6	0.150	2.93
5698	68.7	0.293	3.08	80.8	0.146	2.89
5748	78.1	0.298	3.14	87.2	0.146	2.85
5798	84.2	0.314	3.30	(90.2)	(0.167)	(3.26)

The values of K_i , table 51, show a steady decrease from 5.65×10^{-8} to 2.89×10^{-8} , as the solution becomes less alkaline. The average constant is 3.91×10^{-8} .⁽²⁾ The constants were determined on the assumption that rosolic acid is monobasic; as is well known, the indicator is dibasic, and the decrease in the constants with decreasing alkalinity was expected. Rosolic acid actually dissociates in two stages according to the equations $\text{H}_2\text{In} = \text{HI}\bar{\text{n}} + \text{H}^+$ and $\text{HI}\bar{\text{n}} = \text{I}\bar{\text{n}} + \text{H}^+$.

BEHAVIOR OF ROSOLIC ACID AS A DIBASIC ACID.

As to the two ions $\text{HI}\bar{\text{n}}$ and $\text{I}\bar{\text{n}}$, three assumptions can be made: (1) that the intermediate ion $\text{HI}\bar{\text{n}}$ is yellow and the secondary ion $\text{I}\bar{\text{n}}$ is red; (2) that the ion $\text{HI}\bar{\text{n}}$ is red and the ion $\text{I}\bar{\text{n}}$ is yellow; (3) that both the ions $\text{HI}\bar{\text{n}}$ and $\text{I}\bar{\text{n}}$ are red. In the first case the ratio of the red to the yellow component will be given by

$$c/c_1 = \frac{\text{I}\bar{\text{n}}}{\text{HI}\bar{\text{n}} + \text{H}_2\text{In}} \quad (9)$$

¹The average values of two determinations are given.

²The value given by Salm, in *Zeit. phys. Chem.*, **57**, 496 (1907), is 1.1×10^{-8} .

In addition, the equilibrium equations given below are to be considered:

$$\frac{(\text{H}^+) (\text{HI}\bar{\text{n}})}{(\text{H}_2\text{In})} = K_1 \quad \frac{(\text{H}^+) (\text{I}\bar{\bar{\text{n}}})}{(\text{HI}\bar{\text{n}})} = K_2 \quad (10)$$

By combining these three equations we obtain

$$c/c_1 = \frac{K_1 K_2}{\text{H}^+ (\text{H}^+ + K_1)} \quad (11)$$

In the second case, when the ion $\text{HI}\bar{\text{n}}$ is red and the ion $\text{I}\bar{\bar{\text{n}}}$ is yellow, the ratio becomes

$$c/c_1 = \frac{\text{HI}\bar{\text{n}}}{\text{H}_2\text{In} + \text{I}\bar{\bar{\text{n}}}} \quad (12)$$

and from equation 10

$$c/c_1 = \frac{\text{H}^+ K_1}{\text{H}^2 + K_1 K_2} \quad (13)$$

In the third case, *i. e.*, when both ions $\text{HI}\bar{\text{n}}$ and $\text{I}\bar{\bar{\text{n}}}$ are red, the ratio is given by

$$c/c_1 = \frac{\text{HI}\bar{\text{n}} + \text{I}\bar{\bar{\text{n}}}}{\text{H}_2\text{In}} \quad (14)$$

$$\text{whence, } c/c_1 = \frac{\text{H}^+ K_1 + K_1 K_2}{\text{H}^{+2}} \quad (15)$$

These equations, 11, 13, and 15, were tested by substituting the experimental values of the ratios c/c_1 and the hydrogen ion concentrations given for solutions 1 and 4, table 51, in the equations, and solving for the constants K_1 and K_2 . The constants were then used to calculate the ratios for solutions 2 and 3. Table 52 gives the values of the ratios c/c_1 calculated from the various equations, and also the observed experimental ratios which are the averages of those given in table 51.

TABLE 52.

Solution.	$\text{H}^+ \times 10^3$.	Observed.	Values of c/c .		
			Calc. by 11.	Calc. by 13.	Calc. by 15.
1	2.535	2.23	2.23	2.23	2.230
2	4.484	0.842	1.12		0.953
3	10.53	0.298	0.371		0.308
4	19.52	0.148	0.148	0.148	0.148

On the first assumption, namely, that the ion $\text{HI}\bar{\text{n}}$ is yellow and the ion $\text{I}\bar{\bar{\text{n}}}$ is red, the ratios calculated by equation 11, for solutions 2 and 3, do not at all agree with the experimentally determined values. On the assumption that the intermediate ion $\text{HI}\bar{\text{n}}$ is red and the secondary ion $\text{I}\bar{\bar{\text{n}}}$ is yellow, the constant K_2 , equation 13, was found to be a negative

¹The development is essentially the same as given by Rosenstein for phenolphthalein. Journ. Amer. Chem. Soc., **36**, 1124 (1912).

quantity. This, in itself, proves the absurdity of the assumption; consequently, no ratios for solutions 2 and 3 were calculated. On the assumption, however, that both the ions $\text{HI}\bar{\text{n}}$ and $\text{I}\bar{\text{n}}$ are red, the ratios calculated by equation 15 agree fairly closely with the experimentally determined values. The agreement is as close as could be expected, considering that in work of this character so many different sources of error are possible. The results lead to the conclusion, therefore, that rosolic acid acts as a dibasic acid, and furthermore, show that both the primary and secondary ions are intensely colored.

In the case of phenolphthalein, it has been shown by Rosenstein that the colored form of the indicator is only produced in appreciable quantity where the second hydrogen of the indicator acid is replaced by the base. This is in accordance with the theory already referred to, that the cause of the color production is due to a combination between the metallic phenolate and the quinoid complex, since it is only where the second hydrogen is replaced that the formation of the quinoid phenolate complex is possible. In the case of rosolic acid, however, the quinoid phenolate complex can be found when the first hydrogen of the indicator acid is replaced by the base. The experimental fact, therefore, that the intensely colored form of the indicator is produced when the first hydrogen is replaced by the base, is perfectly in accord with the theories advanced.

SUMMARY.

1. An intensification of the red color of solutions of rosolic acid incompletely transformed by the addition of alkali, was found to take place when such solutions were allowed to stand, the time reaction being in all probability due to a slow union of the metallic phenolate with the quinoid complex.

2. In solutions of rosolic acid containing a large excess of alkali a perceptible bleaching of the red color was also indicated.

3. The ratio (c/c_1) of the red to the yellow component has been determined for indicator solutions of various hydrogen ion concentrations, using the radiometric method developed in the original article.

4. The values of the ionization constant of rosolic acid calculated from the ratio c/c_1 , on the assumption that the indicator acid is monobasic, were found to decrease with decreasing alkalinity. When the hydrogen ion concentration was increased from 2.533×10^{-8} to 19.52×10^{-8} , the total salt concentration being 0.0259 normal, the value of the ionization constant K_i was found to decrease from 5.65×10^{-8} to 2.89×10^{-8} .

5. It was found that this variation in the constants could be explained by regarding the indicator as a dibasic acid, and it was furthermore shown that the intensely colored form of the indicator is formed when the first hydrogen of the indicator acid is replaced by the base.

CHAPTER V.

THE ACTION OF SALTS WITH WATER OF HYDRATION AND WITHOUT WATER OF HYDRATION ON THE VELOCITY OF SAPONIFICATION OF ESTERS.

By J. E. L. HOLMES.

Jones and Anderson,¹ in their work on the absorption spectra of solutions, studied the absorption spectra of neodymium chloride in water, in methyl alcohol, and in mixtures of these two solvents. They found two sets of absorption spectra corresponding, the one to the aqueous solution, the other to the alcoholic. In the mixture of these solvents, both of these spectra were obtained when the water was present in smaller quantities than 15 per cent. With decrease in the percentage of water, the alcoholic spectrum increased in intensity. The water spectrum and the alcohol spectrum were found to be quite different from one another, and do not change over into each other when the composition of the mixed solvent changes.

Similar results were obtained with neodymium nitrate and praseodymium chloride. These results showed that the solvent played an important part in the absorption of light by solutions. Jones and Anderson explained this fact on the basis of the solvate theory of solution proposed by Jones in 1900, that a part of the solvent combines with the dissolved substance and that the solvated parts have different resonance from the unsolvated.

The work of Jones and Anderson was continued by Jones and Strong,² who studied a large number of salts in various solvents, to see if the solvent in general played a rôle in the absorption of light by solution. Most of their work was done with salts of neodymium and uranium, since these substances had sharp absorption lines and bands. That the solvent has much to do with the absorbing power of the solution can be seen from table 53, which contains the wave-lengths of the absorption lines of uranyl chloride in various solvents.

TABLE 53.

In water.....	λλ4025	4170	4315	4460	4560	4740	4920
In methyl alcohol.....	λλ4090	4220	4345	4465	4590	4760	4930
In ethyl alcohol.....	λλ4100	4250		4400	4580	4750	4900
In propyl alcohol.....	λλ4100	4230		4400	4580	4750	4910
In isopropyl alcohol.....	λλ4100	4250		4360	4560	4750	
In butyl alcohol.....	λλ4100	4240		4390	4560	4750	4970
In isobutyl alcohol.....	λλ....			4400	4560	4720	4900
In ether.....	λλ4040	4160		4300	4444		4630
In methyl ester.....	λλ4030	4160	4280	4440	4620	4990	4920
In glycerol.....	λλ4025	4140	4260	4400	4540	4720	5050
In formamid.....	λλ....			4450	4650		4840

¹Carnegie Inst. Wash. Pub. No. 110 (1909); Amer. Chem. Journ., **41**, 163 (1909).

²Carnegie Inst. Wash. Pubs. Nos. **130** (1910) and **160** (1911); Amer. Chem. Journ., **43**, 37, 224 (1910); **45**, 1 (1910); **47**, 27 (1912); Phys. Zeit., **10**, 449 (1909); Phil. Mag., April 1910; Journ. Chim. Phys., **8**, 131 (1910).

Solutions of uranyl chloride in such closely related solvents as propyl and isopropyl alcohols have, as is shown above, different absorption lines and bands.

Jones and Strong studied the absorption spectra of salts of neodymium, and found different absorption lines and bands for solutions of the salts in isomeric solvents. This is brought out in table 54.

TABLE 54.

In water.....	$\lambda\lambda 3390$	3465	3505	3540	3560			
In methyl and ethyl alcohols.....	$\lambda\lambda 3475$	3505		3560				
In propyl alcohol.....	$\lambda\lambda 3545$	3460	3490	3510	3525	3540	3560	3580
In isopropyl alcohol.....	$\lambda\lambda 3460$	3510	3535					
In butyl alcohol.....	$\lambda\lambda 3450$	3460	3492	3535	3545	3560		
In isobutyl alcohol.....	$\lambda\lambda 3455$	3485	3515	3545	3570			
In glycerol.....	$\lambda\lambda 3520$	3475	3550					

The nitrate of neodymium was studied in the same way as the chloride. The absorption bands of neodymium nitrate were found to be practically the same as the absorption bands of neodymium chloride. This is strong evidence that the solvent plays an important part in the absorption of light by substances dissolved in it.

Jones and Strong studied the effect of rise in temperature on the absorption spectra of solutions, and found that the absorption bands widened with rise in temperature. When the solution is cooled down the original spectrum is obtained. This was explained by the initial solvates broken down by rise in temperature being reformed on cooling.

Jones and Guy¹ studied the effect of dilution on absorption spectra, and found that the absorption bands widened as the concentration of the solution was increased. This is what we should expect, since a change in the concentration of the solution would mean a change in the complexity of the solvate. The more dilute the solution the more complex the individual aggregate; and this change in complexity should affect its power of resonance. Conversely, the more concentrated the solution the simpler each individual solvate and the greater its power of resonance.

Jones and Guy studied the effect of the dissolved substance on the absorption of light by water. The absorptions of aqueous solutions of salts were compared with the absorption of a layer of water equal in depth to the water in the solution. Slightly hydrated salts, such as potassium chloride and ammonium chloride, were found to have about the same absorption as water. On the other hand, strongly hydrated salts like calcium and magnesium chlorides, were found to be *far more transparent than pure water*. They explained this fact on the ground that combined water has less absorption than free water.

Jones, Shaeffer, and Paulus² repeated and elaborated the work of Jones and Guy, and found the above relations to be general.

¹Carnegie Inst. Wash. Pub. No. 190 (1913); Ann. der Phys., 43, 555 (1914); Amer. Chem. Journ., 41, 1 (1913).

²Phys. Zeit., 15, 447 (1914).

The above physical difference in the action of combined and of free water, in their power to absorb light, led us to study solutions of slightly hydrated salts and strongly hydrated salts to see if a corresponding chemical difference existed between water in the combined and in the free state—in other words, to study the effect of free water on some chemical reaction in which water is one of the reacting substances, a solution of a slightly hydrated salt containing an amount of water equal to the free water, and a solution of a hydrated salt containing an amount of water equal to the free water.

REACTION CHOSEN.

Berthelot and Péan de Saint Gilles,¹ as early as 1862, showed that the formation of an ester from an alcohol and an acid



proceeded in a slow, progressive manner towards a limit, and that the speed of the reaction was dependent on the amounts of the substances present and on the temperature. This was also shown to be a reversible process.

The reaction of the saponification of an ester has been studied by Ostwald² and Reicher,³ as a method for determining the strengths of acids and bases. Bases were found to saponify the ester more rapidly than acids. The strengths of the acids and bases determined by this method agreed with the strengths as determined by conductivity. In other words, it is the hydroxyl ion of the base and the hydrogen ion of the acid which do the saponifying. The velocities of the reactions studied by Ostwald and Reicher were so much greater, on account of the large number of ions furnished by the acids and bases, in contrast with the small number of ions in those studied by Berthelot and Saint Gilles.

We decided to use the saponification of an ester in the study of the action of *free water* and of *combined water* for the following reasons:

In the first place, as Berthelot and Saint Gilles showed, the speed of the reaction is dependent on the relative amounts of the substances used. By keeping the amount of the ester constant, we could study the effect of the water in solutions of salts containing the same amounts of water.

Secondly, the reaction proceeds slowly and its velocity could therefore be easily measured.

Thirdly, the speed of the reaction is dependent on the temperature. However, as the temperature rises the hydrates become less complex.

¹Ann. Chim. Phys., **65**, 385 (1862); **66**, 5, 110 (1862); **68**, 225, (1865); **14**, 437 (1878); **15**, 220 (1878).

²Jour. prakt. Chem., **28**, 449 (1883); **35**, 112 (1887).

³Lieb. Ann., **228**, 257 (1885).

From the results obtained with the ester and pure water, as compared with those from solutions of the salts, we could study the effect of rise in temperature on the hydrated salts.

HISTORICAL.

The effect of neutral salts on reaction velocities was studied first by Arrhenius,¹ who investigated the hydrolysis of ethyl acetate as effected by bases, and by bases in the presence of one of their salts. He found that in the case of 1/40 normal potassium hydroxide, sodium hydroxide, and barium hydroxide, the addition of their halogen salts decreased the velocity of the reaction, and that the addition of sulphates increased the velocity.

Spohr² studied the effect of neutral salts on the inversion of cane sugar by acids, and on the saponification of an ester by bases. He found that the addition of neutral salts increased the velocity of the former reaction, but diminished the velocity of the latter.

Arrhenius³ also studied the influence of neutral salts on the inversion of cane sugar by acids and obtained results similar to those found by Spohr. The effect of the salt was greater with dilute than with more concentrated acids.

Euler⁴ obtained results very similar to those found by Spohr.

The above work led to the study of the effect of neutral salts when the acid and base were absent.

Smith⁵ measured the dissociation of organic dibasic acids by measuring the rate at which the acids invert cane sugar. He also studied the effect of neutral salts on the reaction when the acids were absent, and found that while salts of weak acids did not affect the reaction differently from pure water, the salts of strong acids, such as potassium chloride and sodium sulphate, produced a large effect.

Kellogg⁶ studied the problem of the effect of neutral salts on the reaction velocity of the saponification of ethyl acetate. The ester and the solutions were sealed in glass tubes and put in a constant-temperature bath at 100°. The tubes were then opened and the contents titrated with phenolphthalein and sodium hydroxide. To get the amounts of the solutions of the salts which should contain an amount of water equal to the free water, the density of the salt solution was determined, its percentage of water content figured, and the amount to be added calculated. Kellogg found that in the more dilute solutions the specific influence of the salt is greater. As the solutions become more concentrated the increase in reaction velocity grows less, and in the case of 4-normal potassium chloride the hydrolysis is slower than in pure water. He found a decrease in the accelerating power from potassium chloride, to potassium bromide, to potassium iodide, which is in the

¹*Zeit. phys. Chem.*, **1**, 110 (1887).

²*Ibid.*, **2**, 194 (1888).

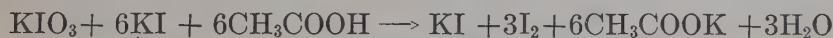
³*Ibid.*, **4**, 237 (1889).

⁴*Ibid.*, **32**, 348 (1900).

⁵*Ibid.*, **25**, 144 (1898).

⁶*Journ. Amer. Chem. Soc.*, **31**, 403, 886 (1909).

reverse order of their stability. The curves plotted with time and percentage hydrolysis as axes are of the same general character, with a concentration of maximum accelerating power, which is 1.8 normal for potassium chloride, 0.5 normal for potassium bromide, and 0.25 normal for potassium iodide. Abnormally low results were found with potassium iodide, which he explained as due to the decomposition of the potassium iodate present by the acetic acid formed in the reaction



These solutions were found to be slightly colored, due to the iodine set free. By varying the time, Kellogg studied the reaction from the point where 1 per cent of the ester was hydrolyzed to practically complete hydrolysis. The salt has two effects, the one in dilute solution being accelerating, the other increasing as the concentration increases, retarding the reaction.

Kellogg made three suggestions to explain this phenomenon. One hypothesis is that the accelerating effect is due to the ionized salt and the retardation is due to the undissociated salt. This would explain the decreasing acceleration with increasing concentration, as the ionized part increases slowly in proportion to the non-ionized part. It would also account for the facts found by the earlier investigators, that the salt of an acid has the greatest effect with dilute acids, since with a dilute acid we have a smaller number of common ions and therefore a greater dissociation of the salt.

Kellogg also stated that the two effects might be functions of the ions; one of the potassium, the other of the halogen ion. This would account for the difference between the three salts which he used, but not for the difference between weak and strong solutions.

Euler's¹ suggestion would explain the dual effect. He assumes that the salt increases the reactive capacity of the water; the ions of the neutral salt combining with the solvent. The water around the ion of the salt is at a high tension, and we therefore would have a large number of $\overset{+}{\text{H}}$ and $\overset{-}{\text{OH}}$ ions. This would explain the larger effect of neutral salts with dilute acids. Spohr and Arrhenius held practically the same views as Euler.

Euler also suggested that intermediate compounds might be formed.

Arrhenius's older idea of the "active" and "inactive" forms of the ester would explain all of the facts, the salt disturbing the equilibrium in favor of the "active" form.

In conclusion, Kellogg stated that no one theory could explain all of the facts, each having its merits and its disadvantages.

Henderson and Kellogg,² continuing the work of Kellogg, studied the chlorides of sodium, lithium, calcium, strontium, and barium, and the

¹*Zeit. phys. Chem.*, **32**, 348 (1900).

²*Journ. Amer. Chem. Soc.*, **35**, 396 (1913).

chloride and iodide of cadmium. They measured the conductivity and viscosity of the solutions at the concentrations and temperature employed in the experiments, and from these calculated the degree of ionization.

The work was carried out under the same conditions employed by Kellogg. They found that all of the salts used, even at concentrations as low as 0.1 normal, increase the rate of the reaction. As the concentration of the salt increases the effect becomes less and, finally, when the solution becomes concentrated, the salt has a retarding effect.

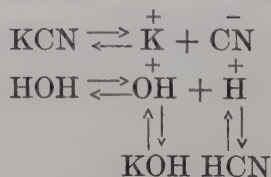
The curves they obtained for these salts were found to be very similar to those for the alkali chlorides, but showed a larger effect. Cadmium chloride and iodide were found to give a very large value, due probably to their hydrolysis, since they have an acid reaction.

Henderson and Kellogg found that the salts which produced the greatest effect were those that were least ionized. From this they drew the conclusion that the solution of the problem was to be sought in the effect of the non-ionized portion of the salt rather than in the ionized portion. If the hydrolysis of the ester is controlled by the concentration of the salt molecules, the cause of the observed maximum¹ is easily explained, since as the total concentration of the salt increases, not only does the concentration of the molecules increase, but the viscosity also varies. The maximum, then, was the resultant between the acceleration produced by the salt molecules which increases with the concentration, and the resistance to the contact of the ester and water, due to the increasing viscosity.

Measurements of the $\overset{+}{\text{H}}$ and $\overset{-}{\text{OH}}$ ions, had they been carried out, would have had an important bearing on Euler's² hypothesis; that at higher salt concentrations water is much more ionized than in dilute solutions, and it is the increase in the ions from water that accelerates the reaction.

HYDROLYSIS.

The presence of hydrogen or hydroxyl ions other than those from water must be guarded against with greatest care. Since the ions from water are relatively so few in number, the introduction of ions from other sources would render the results of little value. Ions might easily be introduced in the ester and in the solutions of the salts. The ester must be distilled until it gives a neutral reaction. Salts of weak acids or weak bases can not be used on account of hydrolysis:



¹Journ. Amer. Chem. Soc., **31**, 886 (1909).

²Zeit. phys. Chem., **32**, 348 (1900).

The hydrocyanic acid would dissociate very slightly, while the potassium hydroxide would be almost entirely dissociated, giving a large excess of OH ions, and therefore an alkaline reaction. The hydroxyl ions, being in large numbers as compared with the hydroxyl ions from the water, would vitiate the results. In the case of a salt of a weak base we would find an acid reaction.

The hydrolysis of salts can be calculated from the formula of Arrhenius,¹

$$\frac{(\text{Salt})}{(\text{Acid}) \times (\text{Base})} = \frac{K \text{ acid}}{K \text{ OH}}$$

in which the salt, acid, and base represent the total concentrations, ionized, and non-ionized, at the point of equilibrium; and the K's are the ionization constants. Similar formulæ were worked out by Walker² for a salt of a weak base and a strong acid, and by Arrhenius for a salt of a weak acid and a weak base.

Where the ionization constant can not be determined by conductivity measurements, other methods must be used.

Shields³ employed the saponification of ethyl acetate and showed that with increasing dilution the hydrolysis increased.

Ley⁴ used the saponification of methyl acetate, the inversion of cane sugar, and the conductivity methods; he found that these three methods gave results which agreed very well with one another. These being the most general methods, are the only ones that need to be considered.

Since the reaction of the saponification of an ester has been used to measure the hydrolysis of salts such as potassium cyanide and aluminum chloride, which react basic and acidic with indicators, it is of primary importance that neutral salts be used.

Salts which give no reaction with litmus, according to Salm,⁵ have a concentration of $\overset{+}{\text{H}}$ or $\overset{-}{\text{OH}}$ ions less than 0.000001, which is so small that it is practically negligible.

We found that the salts of potassium, sodium, lithium, magnesium, calcium, barium, and strontium, with chlorine, bromine, iodine and the nitric and sulphuric acid anions, gave no reaction with litmus. The acids have an ionization constant which is very nearly unity; and the weakest of the bases has so large a constant that if substituted in Walker's formula the hydrolysis would be negligible.

Finally, Bruner⁶ showed that the hydrolysis of solutions of the chlorides of potassium, lithium, barium, strontium, calcium, and magnesium was too small to be measured. He also pointed out that, in general, chlorides were most hydrolyzed, then nitrates, and least of all sulphates.

Therefore, in the solutions to be studied the effect due to hydrolysis may be neglected.

¹Zeit. phys. Chem., **5**, 16 (1890).

²Ibid., **4**, 319 (1889).

³Ibid., **12**, 167 (1893).

⁴Ibid., **30**, 193 (1899).

⁵Ibid., **57**, 471 (1907).

⁶Ibid., **32**, 133 (1900).

STATEMENT OF PROBLEM.

The plan was to investigate the difference in the velocities with which free water and combined water saponified an ester under the following conditions:

(1) Time and concentration of the salts kept constant, temperature varying.

(2) Concentration of the salts and temperature constant, time varying.

(3) Time and temperature constant, concentration of salts varying.

The conditions were so regulated that the percentage of ester saponified was always small, the H^+ ions of the acid formed, being in relatively large numbers as compared with the H^+ ions from water, would suppress the ionization of water and themselves effect the saponification.

EXPERIMENTAL.

APPARATUS.

The reactions were allowed to take place in 100 c.c. Jena bottles with ground-glass stoppers. These bottles were suspended in constant-temperature baths, very similar to those employed by Davis and Putnam.¹ The thermometers were compared with a standardized thermometer. The temperatures of the baths were kept constant to within 0.02 of a degree. The baths were stirred at first by a gas-engine, later by an electric motor. The solutions were measured by means of carefully calibrated pipettes; 10 c.c. burettes were used for measuring the ester, and 50 c.c. burettes for titration purposes. All measuring flasks were made of Jena glass and were calibrated by weight. The solutions were always kept in Jena bottles.

SOLUTIONS.

As stated before, only solutions which gave neutral reactions with litmus were used. The salts were Kahlbaum preparations recrystallized. The solutions of slightly hydrated salts were made up by weight, the strongly hydrated salts by analysis and dilution to the required normality.

A concentration was chosen arbitrarily, such that solutions of all the salts to be investigated could be obtained, *i. e.*, 2 normal. Later it was found to be necessary to change this concentration to normal, using also the more dilute solutions, half-normal and quarter-normal. The amount of the solution that contained an amount of water equal to the free water was determined as follows: 10 c.c. of the solution was weighed and from this the weight of 1 c.c. was determined. The weight of the

¹Carnegie Inst. Wash. Pub. No. 210, 117 (1915).

salt per cubic centimeter was subtracted from this weight, giving the weight of the water per cubic centimeter of the salt solution. By taking the reciprocal of this, the amount of the solution containing an amount of water equal to 1 c.c. was obtained. The same trouble was found with solutions of potassium iodide and sodium iodide being colored, as Kellogg¹ describes. A drop of sodium thiosulphate was used to decolorize the solution before titrating, as the color obscured the change in the indicator. All solutions of the halogens were standardized as their silver salts. Calcium nitrate was converted into the oxide, magnesium nitrate into the pyrophosphate, strontium nitrate into the sulphate, and lithium nitrate into the sulphate by evaporating with sulphuric acid. Magnesium sulphate was standardized as barium sulphate, and the iodides of sodium and potassium were also determined gravimetrically.

THE ESTERS.

The ester first employed was ethyl acetate. After some preliminary work, this was discarded in favor of methyl acetate, since its solubility in some of the strong salt solutions was so slight as to give us a heterogeneous system. Methyl formate was also studied, to see if the results obtained with methyl acetate were of a general character or specific to the ester in question. The esters, which were Kahlbaum preparations, were distilled several times until they boiled at the proper temperature and their reaction was neutral. The methyl formate had to be distilled frequently, on account of its apparent instability.

THE BASE AND THE INDICATOR.

The finding of the proper base and indicator to be used in titrating the acid formed gave us quite a little trouble. Standard sulphuric acid was made up, and on analysis found to contain 0.01205 gram of sulphuric acid per cubic centimeter. This was used to standardize the base, the comparison being repeated from time to time to see that the base did not undergo any change in concentration. The acid was also restandardized from time to time, no change in its concentration being noticed. The alkali used first was alcoholic sodium hydroxide; the indicator was phenolphthalein. The precipitate of sodium carbonate was filtered from the alcoholic solution in an atmosphere free from carbon dioxide, by a method similar to that employed by Morse.² The alkali was one-tenth normal. Great difficulty was experienced in obtaining good end-points with the above base and indicator. This might be due to the saponification of the ester by the strong base, or to the unfitness of the indicator. We therefore decided to test out different indicators and bases.

¹Journ. Amer. Chem. Soc., **31**, 886 (1909).

²Exercises in Quant. Chem., 330.

We obtained the following results:

Ammonia and phenolphthalein:

- 10 c.c. standard acid in presence of the ester—19.3 c.c. of base used.
- 10 c.c. standard acid—16.3 c.c. of base.

Sodium hydroxide and phenolphthalein:

- 5 c.c. H_2SO_4 , strength unknown in presence of the ester—16.8 c.c. of base used.
- 5 c.c. H_2SO_4 , strength unknown—13.60 c.c. of base.

Ammonia and methyl orange:

- 5 c.c. standard acid in presence of the ester—7.8 c.c. of base used.
- 5 c.c. standard acid—7.82 c.c. of base.

Sodium hydroxide and methyl orange:

- 5 c.c. standard acid in presence of the ester—12.60 c.c. of base used.
- 5 c.c. standard acid—12.55 c.c. of base.

Sodium hydroxide and methyl orange:

- 5 c.c. H_2SO_4 , strength unknown in presence of the ester—14.5 c.c. of base used.
- 5 c.c. H_2SO_4 , strength unknown—13.5 c.c. of base.

Ammonia and methyl orange:

- 5 c.c. H_2SO_4 , strength unknown in presence of the ester—8.7 c.c. of base used.
- 5 c.c. H_2SO_4 , strength unknown—8.6 c.c. of base.

Ammonia and phenolphthalein:

- 5 c.c. H_2SO_4 , strength unknown in presence of the ester—9.4 c.c. of base used.
- 5 c.c. H_2SO_4 , strength unknown—9.1 c.c. of base.

Thus far, ammonia and methyl orange gave the best results. With sodium hydroxide the color of the indicator rapidly disappears on standing, due probably to saponification of the ester. Barium hydroxide has frequently been used for this purpose; therefore we tried this base.

Barium hydroxide and phenolphthalein:

- 5 c.c. H_2SO_4 , strength unknown in presence of the ester—6.0 c.c. of base used.
- 5 c.c. H_2SO_4 , strength unknown—5.8 c.c. of base.

Barium hydroxide and methyl orange:

- 5 c.c. H_2SO_4 , strength unknown in presence of the ester—5.8 c.c. of base used.
- 5 c.c. H_2SO_4 , strength unknown—5.7 c.c. of base.

The color of the indicator did not persist with barium hydroxide. Therefore, we discarded this in favor of ammonium hydroxide. As regards acetic acid, methyl orange is the only common indicator that can be used.

Ammonia and methyl orange:

- 10 c.c. acetic acid, strength unknown in presence of ester—0.2 c.c. of base used.
- 10 c.c. acetic acid, strength unknown—0.1 c.c. of base.

Methyl orange is of little value, since we should have obtained readings of about 8 or 10 c.c. Morse suggests carollin, since this is a good indicator with organic acids.¹

Ammonia and corallin:

- 10 c.c. acetic acid, strength unknown in presence of ester—
- 9.0 c.c. base used.
- 9.0 c.c. base used.
- 10 c.c. acetic acid, strength unknown—
- 9.1 c.c. of base.
- 9.1 c.c. of base.

¹Morse: Exercises in Quant. Chem., 289; Glaser: Indikatoren, 92.

To see if the addition of salts would have any effect on the titration, we titrated in the presence of the ester and a salt:

10 c.c. acetic acid, strength unknown:

In presence of the ester and calcium chloride; 9.05 c.c. of base used.

In presence of the ester and potassium chloride; 9.0 c.c. of base used.

Ammonium hydroxide and alcoholic corallin are, then, the base and the indicator to be used.

At first one-fifth normal ammonia was used, but this gave us such small volumes that we decided to use one-twentieth normal.

After preparing the solution of the base, it was found to be not quite one-twentieth normal, but to contain 0.00167732 gram per c.c.

For use with the methyl formate a fifth-normal solution was made up which contained 0.007 gram per c.c.

To see if the methods we were using were accurate, the following experiments were carried out:

0.0733 gram of glacial acetic acid was weighed out and titrated with ammonia, corallin being used as the indicator. The amount of acetic acid calculated from the titration was 0.0730 gram. We would then have an error of less than 0.5 per cent. With other organic acids we found errors of less than 0.1 per cent.

The results obtained with formic acid of about 98.5 per cent purity were 0.4917 gram weighed out, and 0.4842 gram was calculated from the titration, giving us an error of about 0.1 per cent.

METHOD OF PROCEDURE.

Solutions of the salts and the ester were measured into bottles, which were then placed in the baths. After the required time had elapsed, the bottles were removed from the baths, and their contents titrated against the standard base. We found, after a good deal of preliminary experimenting, that the most favorable conditions for work were: for the methyl acetate, 4 c.c. of the ester to 30 c.c. of water, 24 and 48 hours, 15, 25, and 35 degrees, and normal, half-normal, and quarter-normal salt solutions. For the methyl formate, 2 c.c. of the ester to 30 c.c. of water, 4 and 8 hours, 15 and 25 degrees (b. p. of methyl formate—32.3°) and the same concentrations of the salts as were used with the methyl acetate. The bottles, when taken out of the baths, were immediately chilled to retard the reaction. The time required for titrating was practically the same as that for adding the ester; therefore, the results are comparable. 12 solutions were studied at a time, 6 being duplicates; 2 bottles containing pure water and ester were included in the sets of 12 bottles, to act as standards and to show that the conditions did not vary. The addition of the ester and the titration of the contents of the bottles were always carried on in the same order; *e. g.*, the bottle to which the ester was added was titrated first. The methyl formate had to be measured at

15°, on account of its high vapor-tension. At first the titration was made in beakers; later it was found that the titration could be carried on very well in the bottle itself, thus eliminating a source of error. An electric motor was used for stirring the baths, since the hot-air engine could not be run over night. When the baths were not stirred during the night, they varied as much as 0.3° or 0.4°; and the position of the bottles as regards the heating and cooling surfaces seemed to produce a marked effect. Normal solutions of sodium and potassium sulphates and of barium nitrate could not be prepared, since these salts were not sufficiently soluble; therefore, they were not studied. Cadmium and aluminum salts were discarded on account of their acid reaction, and ammonium salts because they suppressed to nearly half-value the ionization of the alkali used in the titration. The ammonium salt formed by the neutralization of the acid titrated with the base would also affect the ionization of the base, if the reaction was allowed to proceed very far.

CALCULATIONS.

The results are expressed in percentages of the ester decomposed. This was obtained as follows:

In the first place the total amount of the ester per bottle was determined. From the mean weight of four 10 c.c. portions the weight per cubic centimeter of the methyl acetate was found to be 0.9257 gram, giving us 3.7028 grams as the total weight of the methyl acetate.

Then the weight of the ester, which, on saponification, would give enough acetic acid to neutralize 1 c.c. of the standard one-twentieth normal ammonia, was calculated; 1 c.c. of ammonia corresponded to a decomposition of 0.003543 gram of methyl acetate. Dividing this value by the total amount of the ester, 3.7028 grams, we find that 1 c.c. of one-twentieth normal ammonia (0.001677 gram per c.c.) represents 0.0957 per cent of the ester saponified.

To get the percentage saponification for each salt, it is only necessary to multiply the burette reading for each bottle by the factor 0.0957 per cent.

For methyl formate we obtained the following values: The weight per c.c. of ester, 0.9701 gram; the total weight of the ester, 1.9402 grams; the weight of the ester which, when saponified, corresponded to 1 c.c. of the fifth-normal ammonia (per c.c. 0.007 gram) is 0.01199 gram, and the percentage saponification, 0.618 per cent.

DATA.

In the following tables of data, the methyl acetate per bottle is 4 c.c. or 3.7028 grams; the methyl formate, 2 c.c. or 1.9402 grams. Table 56 contains the results when the baths were not stirred over night, and these results have, therefore, a slight error. It was found that calcium chloride and potassium nitrate, on dilution, increase, then decrease the velocity of the reaction. Duplicate measurements were, therefore, made with new solutions, and the results recorded in table 58. The

data in tables 64 and 65 were obtained, using the same salt solutions. It was at this point that we decided to study also methyl formate. For tables 67 and 69 new solutions were used, since those earlier employed had not been preserved. The volumes of the solutions of the salts that contained 30 c.c. of water were calculated as described above, the water per cubic centimeter of the solution being the difference in weight between 1 c.c. of the solution and the salt in 1 c.c. The water used in preparing the solutions of the salts, bases, and acid had been carefully purified, and had a mean specific conductivity of 1.5×10^{-6} at 25° . This water was also employed in recrystallizing the salts. In the tables of data the concentrations of the solutions of the salts are expressed as N, N/2, and N/4. Tables 56, 58, 60, 62, and 64 give the percentages of the methyl acetate saponified; tables 65, 67, and 69 of the methyl formate. Duplicate measurements were made with fresh solutions of magnesium sulphate and strontium bromide; since the results obtained with these salts were very low as compared with the results from the other salts that contain a large amount of water of crystallization. The results found were, however, identical with those earlier obtained.

TABLE 55.

Solutions of the salts.	Grams of H ₂ O per c.c. of the solution.	Volume of solution cont. ¹ 1 c.c. H ₂ O.	Volume of solution cont. 30 c.c. H ₂ O.	Solutions of the salts.	Grams of H ₂ O per c.c. of the solution.	Volume of solution cont. 1 c.c. H ₂ O.	Volume of solution cont. 30 c.c. H ₂ O.
N KCl.....	0.9717	1.029	30.87	N/2 MgCl ₂	0.9874	1.013	30.39
N KNO ₃	0.9610	1.041	31.23	N/2 SrCl ₂	0.9852	1.015	30.45
N CaCl ₂	0.9721	1.028	30.84	N/4 KCl.....	0.9910	1.009	30.27
N MgCl ₂	0.9806	1.020	30.60	N/4 KNO ₃	0.9845	1.016	30.48
N SrCl ₂	0.9716	1.029	30.87	N/4 CaCl ₂	0.9921	1.008	30.24
N/2 KCl.....	0.9846	1.016	30.48	N/4 MgCl ₂	0.9924	1.008	30.24
N/2 KNO ₃	0.9789	1.022	30.66	N/4 SrCl ₂	0.9909	1.009	30.27
N/2 CaCl ₂	0.9871	1.013	30.39				

TABLE 56.

No.	Solutions N.	15° 24 hrs.	25° 24 hrs.	35° 24 hrs.	25° 48 hrs.	Solutions N/2.	25° 24 hrs.	35° 24 hrs.	Solutions N/4.	25° 24 hrs.
1	{ 30 c.c. }	0.076	0.147	0.390	0.287	{ 30 c.c. }	0.145	0.386	{ 30 c.c. }	0.153
2	{ H ₂ O. }	0.076	0.145	0.392	0.289	{ H ₂ O. }	0.144	0.385	{ H ₂ O. }	0.152
3	{ 30.87 c.c. }	0.100	0.224	0.720	0.516	{ 30.48 c.c. }	0.206	0.669	{ 30.27 c.c. }	0.196
4	{ KCl. }	0.100	0.222	0.722	0.513	{ KCl. }	0.206	0.666	{ KCl. }	0.198
5	{ 31.23 c.c. }	0.099	0.194	0.611	0.431	{ 30.66 c.c. }	0.201	0.612	{ 30.48 c.c. }	0.177
6	{ KNO ₃ . }	0.097	0.196	0.614	0.431	{ KNO ₃ . }	0.201	0.613	{ KNO ₃ . }	0.177
7	{ 30.84 c.c. }	0.119	0.387	1.68	1.03	{ 30.39 c.c. }	0.400	1.35	{ 30.24 c.c. }	0.278
8	{ CaCl ₂ . }	0.117	0.385	1.69	1.05	{ CaCl ₂ . }	0.398	1.36	{ CaCl ₂ . }	0.277
9	{ 30.60 c.c. }	0.132	0.410	1.67	1.33	{ 30.39 c.c. }	0.326	1.23	{ 30.24 c.c. }	0.276
10	{ MgCl ₂ . }	0.134	0.411	1.67	1.30	{ MgCl ₂ . }	0.323	1.23	{ MgCl ₂ . }	0.276
11	{ 30.87 c.c. }	0.130	0.378	1.41	0.992	{ 30.45 c.c. }	0.297	1.12	{ 30.27 c.c. }	0.236
12	{ SrCl ₂ . }	0.128	0.375	1.42	0.989	{ SrCl ₂ . }	0.297	1.12	{ SrCl ₂ . }	0.239

¹ "Cont." in this and the following tables is "containing."

TABLE 57.

Solutions of the salts.		Grams of H ₂ O per c.c. of the solution.	Volume of solution cont. 1 c.c. H ₂ O.	Volume of solution cont. 30 c.c. H ₂ O.	Solutions of the salts.		Grams of H ₂ O per c.c. of the solution.	Volume of solution cont. 1 c.c. H ₂ O.	Volume of solution cont. 30 c.c. H ₂ O.
N	LiCl.....	0.9688	1.032	30.96	N/2	CaCl ₂	0.9868	1.013	30.39
N	KNO ₃	0.9589	1.043	31.29	N/2	Ca(NO ₃) ₂	0.9773	1.023	30.69
N	NaCl.....	0.9811	1.019	30.57	N/4	LiCl.....	0.9917	1.008	30.24
N	CaCl ₂	0.9718	1.029	30.87	N/4	KNO ₃	0.9870	1.013	30.39
N	Ca(NO ₃) ₂	0.9496	1.053	31.59	N/4	NaCl.....	0.9931	1.007	30.21
N/2	LiCl.....	0.9840	1.016	30.48	N/4	CaCl ₂	0.9909	1.009	30.27
N/2	KNO ₃	0.9802	1.020	30.60	N/4	Ca(NO ₃) ₂	0.9880	1.012	30.36
N/2	NaCl.....	0.9903	1.010	30.30					

TABLE 58.

No.	Solutions N.	15° 24 hrs.	25° 24 hrs.	35° 24 hrs.	25° 48 hrs.	Solutions N/2.	25° 24 hrs.	35° 24 hrs.	Solutions N/4.	25° 24 hrs.
1	{ 30 c.c. }	0.083	0.154	0.394	0.296	{ 30 c.c. }	0.153	0.391	{ 30 c.c. }	0.152
2	{ H ₂ O. }	0.084	0.154	0.392	0.297	{ H ₂ O. }	0.153	0.390	{ H ₂ O. }	0.151
3	{ 30.96 c.c. }	0.094	0.204	0.626	0.462	{ 30.48 c.c. }	0.199	0.590	{ 30.24 c.c. }	0.194
4	{ LiCl. }	0.093	0.203	0.624	0.464	{ LiCl. }	0.198	0.591	{ LiCl. }	0.194
5	{ 31.29 c.c. }	0.099	0.215	0.631	0.457	{ 30.60 c.c. }	0.213	0.632	{ 30.39 c.c. }	0.212
6	{ KNO ₃ . }	0.100	0.214	0.633	0.456	{ KNO ₃ . }	0.212	0.634	{ KNO ₃ . }	0.211
7	{ 30.57 c.c. }	0.109	0.247	0.808	0.590	{ 30.30 c.c. }	0.241	0.746	{ 30.21 c.c. }	0.222
8	{ NaCl. }	0.111	0.245	0.806	0.591	{ NaCl. }	0.242	0.745	{ NaCl. }	0.222
9	{ 30.87 c.c. }	0.129	0.393	1.72	1.15	{ 30.39 c.c. }	0.306	1.35	{ 30.27 c.c. }	0.285
10	{ CaCl ₂ . }	0.131	0.395	1.71	1.16	{ CaCl ₂ . }	0.308	1.36	{ CaCl ₂ . }	0.284
11	{ 31.59 c.c. }	0.129	0.330	1.32	0.860	{ 30.69 c.c. }	0.310	1.12	{ 30.36 c.c. }	0.270
12	{ Ca(NO ₃) ₂ . }	0.126	0.333	1.34	0.861	{ Ca(NO ₃) ₂ . }	0.308	1.12	{ Ca(NO ₃) ₂ . }	0.269

TABLE 59.

Solutions of the salts.		Grams of H ₂ O per c.c. of the solution.	Volume of solution cont. 1 c.c. H ₂ O.	Volume of solution cont. 30 c.c. H ₂ O.	Solutions of the salts.		Grams of H ₂ O per c.c. of the solution.	Volume of solution cont. 1 c.c. H ₂ O.	Volume of solution cont. 30 c.c. H ₂ O.
N	NaNO ₃	0.9696	1.031	30.93	N/2	BaCl ₂	0.9842	1.016	30.48
N	NaBr.....	0.9728	1.028	30.84	N/2	Mg(NO ₃) ₂	0.9789	1.022	30.66
N	KBr.....	0.9642	1.037	31.11	N/4	NaNO ₃	0.9881	1.012	30.36
N	BaCl ₂	0.9700	1.031	30.93	N/4	NaBr.....	0.9922	1.008	30.24
N	Mg(NO ₃) ₂	0.9527	1.049	31.48	N/4	KBr.....	0.9868	1.013	30.39
N/2	NaNO ₃	0.9803	1.020	30.60	N/4	BaCl ₂	0.9917	1.008	30.24
N/2	NaBr.....	0.9852	1.015	30.45	N/4	Mg(NO ₃) ₂	0.9877	1.012	30.36
N/2	KBr.....	0.9804	1.020	30.60					

TABLE 60.

No.	Solutions N.	15° 24 hrs.	25° 24 hrs.	35° 24 hrs.	25° 48 hrs.	Solutions N/2.	25° 24 hrs.	35° 24 hrs.	Solutions N/4.	25° 24 hrs.
1	{ 30 c.c. H ₂ O. }	0.086	0.155	0.394	0.296	{ 30 c.c. H ₂ O. }	0.153	0.394	{ 30 c.c. H ₂ O. }	0.153
2	{ 30.93 c.c. NaNO ₃ . }	0.086	0.154	0.395	0.297	{ 30.60 c.c. NaNO ₃ . }	0.155	0.393	{ 30.36 c.c. NaNO ₃ . }	0.154
3	{ 30.84 c.c. NaBr. }	0.105	0.225	0.692	0.490	{ 30.45 c.c. NaBr. }	0.223	0.663	{ 30.24 c.c. NaBr. }	0.210
4	{ 31.11 c.c. KBr. }	0.105	0.224	0.691	0.488	{ 30.60 c.c. KBr. }	0.222	0.661	{ 30.39 c.c. KBr. }	0.211
5	{ 30.93 c.c. BaCl ₂ . }	0.104	0.228	0.703	0.517	{ 30.48 c.c. BaCl ₂ . }	0.222	0.660	{ 30.24 c.c. BaCl ₂ . }	0.210
6	{ 31.48 c.c. Mg(NO ₃) ₂ . }	0.105	0.227	0.704	0.517	{ 30.66 c.c. Mg(NO ₃) ₂ . }	0.223	0.661	{ 30.39 c.c. Mg(NO ₃) ₂ . }	0.209
7		0.107	0.230	0.690	0.507		0.224	0.667		0.216
8		0.106	0.231	0.689	0.505		0.224	0.668		0.217
9		0.142	0.377	1.38	0.967		0.315	1.09		0.267
10		0.144	0.377	1.37	0.965		0.316	1.09		0.268
11		0.125	0.326	1.35	0.883		0.285	1.13		0.261
12		0.126	0.325	1.36	0.885		0.286	1.14		0.263

TABLE 61.

Solutions of the salts.	Grams of H ₂ O per c.c. of the solution.	Volume of solu- tion cont. 1 c.c. H ₂ O.	Volume of solu- tion cont. 30 c.c. H ₂ O.	Solutions of the salts.	Grams of H ₂ O per c.c. of the solution.	Volume of solu- tion cont. 1 c.c. H ₂ O.	Volume of solu- tion cont. 30 c.c. H ₂ O.
N KI.....	0.9513	1.051	31.53	N/2 MgSO ₄	0.9950	1.005	30.15
N NaI.....	0.9611	1.040	31.20	N/2 Sr(NO ₃) ₂	0.9758	1.025	30.75
N CaBr ₂	0.9597	1.042	31.26	N/4 KI.....	0.9864	1.014	30.42
N MgSO ₄	0.9938	1.006	30.18	N/4 NaI.....	0.9904	1.010	30.30
N Sr(NO ₃) ₂	0.9509	1.052	31.56	N/4 CaBr ₂	0.9891	1.011	30.33
N/2 KI.....	0.9746	1.026	30.78	N/4 MgSO ₄	0.9958	1.004	30.12
N/2 NaI.....	0.9809	1.019	30.57	N/4 Sr(NO ₃) ₂	0.9881	1.012	30.36
N/2 CaBr ₂	0.9825	1.018	30.54				

TABLE 62.

No.	Solutions N.	15° 24 hrs.	25° 24 hrs.	35° 24 hrs.	25° 48 hrs.	Solutions N/2.	25° 24 hrs.	35° 24 hrs.	Solutions N/4.	25° 24 hrs.
1	{ 30 c.c. H ₂ O. }	0.086	0.155	0.395	0.296	{ 30 c.c. H ₂ O. }	0.155	0.395	{ 30 c.c. H ₂ O. }	0.155
2	{ 31.53 c.c. KI. }	0.086	0.155	0.394	0.296	{ 30.78 c.c. KI. }	0.155	0.394	{ 30.42 c.c. KI. }	0.154
3	{ 31.20 c.c. NaI. }	0.030	0.038	0.057	0.048	{ 30.57 c.c. NaI. }	0.073	0.172	{ 30.30 c.c. NaI. }	0.136
4		0.032	0.036	0.056	0.049		0.073	0.172		0.135
5		0.075	0.119	0.341	0.239		0.171	0.498		0.176
6		0.077	0.118	0.342	0.241		0.172	0.498		0.177
7		0.075	0.134	0.653	0.492		0.153	0.689		0.191
8		0.073	0.132	0.651	0.494		0.151	0.671		0.192
9		0.095	0.166	0.406	0.346		0.150	0.372		0.138
10		0.097	0.168	0.408	0.344		0.148	0.374		0.140
11		0.139	0.297	1.09	0.711		0.287	0.968		0.260
12		0.139	0.298	1.09	0.713		0.285	0.966		0.261

TABLE 63.

Solutions of the salts.		Grams of H ₂ O per c.c. of the solution.	Volume of solution cont. 1 c.c. H ₂ O.	Volume of solution cont. 30 c.c. H ₂ O.	Solutions of the salts.		Grams of H ₂ O per c.c. of the solution.	Volume of solution cont. 1 c.c. H ₂ O.	Volume of solution cont. 30 c.c. H ₂ O.
N	LiBr.....	0.9739	1.027	30.81	N/2	SrBr ₂	0.9765	1.024	30.72
N	Li ₂ SO ₄	0.9757	1.025	30.75	N/2	LiNO ₃	0.9825	1.018	30.54
N	BaBr ₂	0.9529	1.049	31.47	N/4	LiBr.....	0.9928	1.007	30.21
N	SrBr ₂	0.9536	1.049	31.47	N/4	Li ₂ SO ₄	0.9940	1.006	30.18
N	LiNO ₃	0.9673	1.034	31.02	N/4	BaBr ₂	0.9871	1.013	30.39
N/2	LiBr.....	0.9849	1.015	30.45	N/4	SrBr ₂	0.9870	1.013	30.39
N/2	Li ₂ SO ₄	0.9882	1.012	30.36	N/4	LiNO ₃	0.9891	1.011	30.33
N/2	BaBr ₂	0.9761	1.025	30.75					

TABLE 64.

No.	Solutions N.	15° 24 hrs.	25° 24 hrs.	35° 24 hrs.	25° 48 hrs.	Solutions N/2.	25° 24 hrs.	35° 24 hrs.	Solutions N/4.	25° 24 hrs.
1	{ 30 c.c. }	0.087	0.153	0.392	0.297	{ 30 c.c. }	0.153	0.392	{ 30 c.c. }	0.153
2	{ H ₂ O. }	0.086	0.153	0.392	0.298	{ H ₂ O. }	0.154	0.392	{ H ₂ O. }	0.153
3	{ 30.81 c.c. }	0.033	0.053	0.128	0.100	{ 30.45 c.c. }	0.105	0.307	{ 30.21 c.c. }	0.161
4	{ LiBr. }	0.033	0.053	0.129	0.099	{ LiBr. }	0.106	0.308	{ LiBr. }	0.160
5	{ 30.75 c.c. }	0.103	0.153	0.306	0.278	{ 30.36 c.c. }	0.149	0.297	{ 30.18 c.c. }	0.139
6	{ Li ₂ SO ₄ . }	0.105	0.153	0.305	0.277	{ Li ₂ SO ₄ . }	0.151	0.299	{ Li ₂ SO ₄ . }	0.139
7	{ 31.47 c.c. }	0.081	0.179	0.705	0.445	{ 30.75 c.c. }	0.223	0.813	{ 30.39 c.c. }	0.241
8	{ BaBr ₂ . }	0.081	0.177	0.707	0.446	{ BaBr ₂ . }	0.224	0.815	{ BaBr ₂ . }	0.239
9	{ 31.47 c.c. }	0.075	0.096	0.250	0.190	{ 30.72 c.c. }	0.130	0.387	{ 30.39 c.c. }	0.164
10	{ SrBr ₂ . }	0.077	0.098	0.248	0.192	{ SrBr ₂ . }	0.128	0.385	{ SrBr ₂ . }	0.162
11	{ 31.02 c.c. }	0.086	0.167	0.508	0.370	{ 30.54 c.c. }	0.182	0.555	{ 30.33 c.c. }	0.201
12	{ LiNO ₃ . }	0.086	0.168	0.510	0.371	{ LiNO ₃ . }	0.182	0.557	{ LiNO ₃ . }	0.200

TABLE 65.

No.	Solutions N.	15° 4 hrs.	25° 4 hrs.	15° 8 hrs.	Solutions N/2.	15° 4 hrs.	Solutions N/4.	15° 4 hrs.
1	{ 30 c.c. }	0.668	3.89	2.58	{ 30 c.c. }	0.680	{ 30 c.c. }	0.667
2	{ H ₂ O. }	0.667	3.90	2.60	{ H ₂ O. }	0.686	{ H ₂ O. }	0.661
3	{ 30.81 c.c. }	0.309	5.26	2.56	{ 30.45 c.c. }	0.650	{ 30.21 c.c. }	0.927
4	{ LiBr. }	0.296	5.24	2.56	{ LiBr. }	0.643	{ LiBr. }	0.939
5	{ 30.75 c.c. }	0.742	3.96	3.80	{ 30.36 c.c. }	0.667	{ 30.18 c.c. }	0.618
6	{ Li ₂ SO ₄ . }	0.742	3.97	3.78	{ Li ₂ SO ₄ . }	0.661	{ Li ₂ SO ₄ . }	0.605
7	{ 31.47 c.c. }	0.754	9.27	4.76	{ 30.75 c.c. }	1.050	{ 30.39 c.c. }	1.420
8	{ BaBr ₂ . }	0.747	9.27	4.76	{ BaBr ₂ . }	1.070	{ BaBr ₂ . }	1.430
9	{ 31.47 c.c. }	0.278	3.47	1.78	{ 30.72 c.c. }	0.590	{ 30.39 c.c. }	0.990
10	{ SrBr ₂ . }	0.279	3.45	1.80	{ SrBr ₂ . }	0.588	{ SrBr ₂ . }	0.988
11	{ 31.02 c.c. }	0.865	6.74	4.44	{ 30.54 c.c. }	1.020	{ 30.33 c.c. }	1.110
12	{ LiNO ₃ . }	0.865	6.72	4.45	{ LiNO ₃ . }	1.020	{ LiNO ₃ . }	1.120

TABLE 66.

Solutions of the salts.		Grams of H ₂ O per c.c. of the solution.	Volume of solution cont. 1 c.c. H ₂ O.	Volume of solution cont. 30 c.c. H ₂ O.	Solutions of the salts.		Grams of H ₂ O per c.c. of the solution.	Volume of solution cont. 1 c.c. H ₂ O.	Volume of solution cont. 30 c.c. H ₂ O.
N	NaBr.....	0.9722	1.029	30.87	N/2	Ca(NO ₃) ₂	0.9772	1.023	30.69
N	KCl.....	0.9704	1.030	30.90	N/2	MgSO ₄	0.9950	1.005	30.15
N	BaCl ₂	0.9703	1.031	30.93	N/4	NaBr.....	0.9928	1.007	30.21
N	Ca(NO ₃) ₂	0.9494	1.053	31.59	N/4	KCl.....	0.9912	1.009	30.27
N	MgSO ₄	0.9938	1.006	30.18	N/4	BaCl ₂	0.9922	1.008	30.24
N/2	NaBr.....	0.9866	1.014	30.42	N/4	Ca(NO ₃) ₂	0.9883	1.012	30.36
N/2	KCl.....	0.9850	1.015	30.45	N/4	MgSO ₄	0.9958	1.004	30.12
N/2	BaCl ₂	0.9842	1.016	30.48					

TABLE 67.

No.	Solutions N.	15° 4 hrs.	25° 4 hrs.	15° 8 hrs.	Solutions N/2.	15° 4 hrs.	Solutions N/4.	15° 4 hrs.
1	{ 30 c.c. }	0.661	3.87	2.58	{ 30 c.c. }	0.680	{ 30 c.c. }	0.680
2	{ H ₂ O. }	0.667	3.90	2.60	{ H ₂ O. }	0.680	{ H ₂ O. }	0.680
3	{ 30.87 c.c. }	1.05	7.00	4.25	{ 30.42 c.c. }	0.988	{ 30.21 c.c. }	0.927
4	{ NaBr. }	1.06	6.98	4.26	{ NaBr. }	0.988	{ NaBr. }	0.929
5	{ 30.90 c.c. }	1.11	7.05	4.33	{ 30.45 c.c. }	1.11	{ 30.27 c.c. }	1.05
6	{ KCl. }	1.12	7.06	4.32	{ KCl. }	1.10	{ KCl. }	1.04
7	{ 30.93 c.c. }	1.78	13.71	7.23	{ 30.48 c.c. }	1.71	{ 30.24 c.c. }	1.47
8	{ BaCl ₂ . }	1.76	13.70	7.22	{ BaCl ₂ . }	1.69	{ BaCl ₂ . }	1.45
9	{ 31.59 c.c. }	1.24	9.86	5.25	{ 30.69 c.c. }	1.17	{ 30.36 c.c. }	1.11
10	{ Ca(NO ₃) ₂ . }	1.25	9.84	5.24	{ Ca(NO ₃) ₂ . }	1.19	{ Ca(NO ₃) ₂ . }	1.13
11	{ 30.18 c.c. }	1.36	8.50	5.92	{ 30.15 c.c. }	1.10	{ 30.12 c.c. }	0.926
12	{ MgSO ₄ . }	1.37	8.49	5.94	{ MgSO ₄ . }	1.12	{ MgSO ₄ . }	0.928

TABLE 68.

Solutions of the salts.		Grams of H ₂ O per c.c. of the solution.	Volume of solution cont. 1 c.c. H ₂ O.	Volume of solution cont. 30 c.c. H ₂ O.	Solutions of the salts.		Grams of H ₂ O per c.c. of the solution.	Volume of solution cont. 1 c.c. H ₂ O.	Volume of solution cont. 30 c.c. H ₂ O.
N	KI.....	0.9508	1.052	31.56	N/2	CaCl ₂	0.9870	1.013	30.39
N	CaBr ₂	0.9599	1.042	31.26	N/2	Mg(NO ₃) ₂	0.9787	1.022	30.66
N	SrCl ₂	0.9719	1.029	30.87	N/4	KI.....	0.9864	1.014	30.42
N	CaCl ₂	0.9718	1.029	30.87	N/4	CaBr ₂	0.9894	1.011	30.33
N	Mg(NO ₃) ₂	0.9529	1.049	31.48	N/4	SrCl ₂	0.9914	1.009	30.27
N/2	KI.....	0.9741	1.027	30.81	N/4	CaCl ₂	0.9912	1.009	30.27
N/2	CaBr ₂	0.9823	1.018	30.54	N/4	Mg(NO ₃) ₂	0.9877	1.012	30.36
N/2	SrCl ₂	0.9852	1.015	30.45					

The following curves show the percentages of methyl acetate saponified at 15°, 25° and 30°.

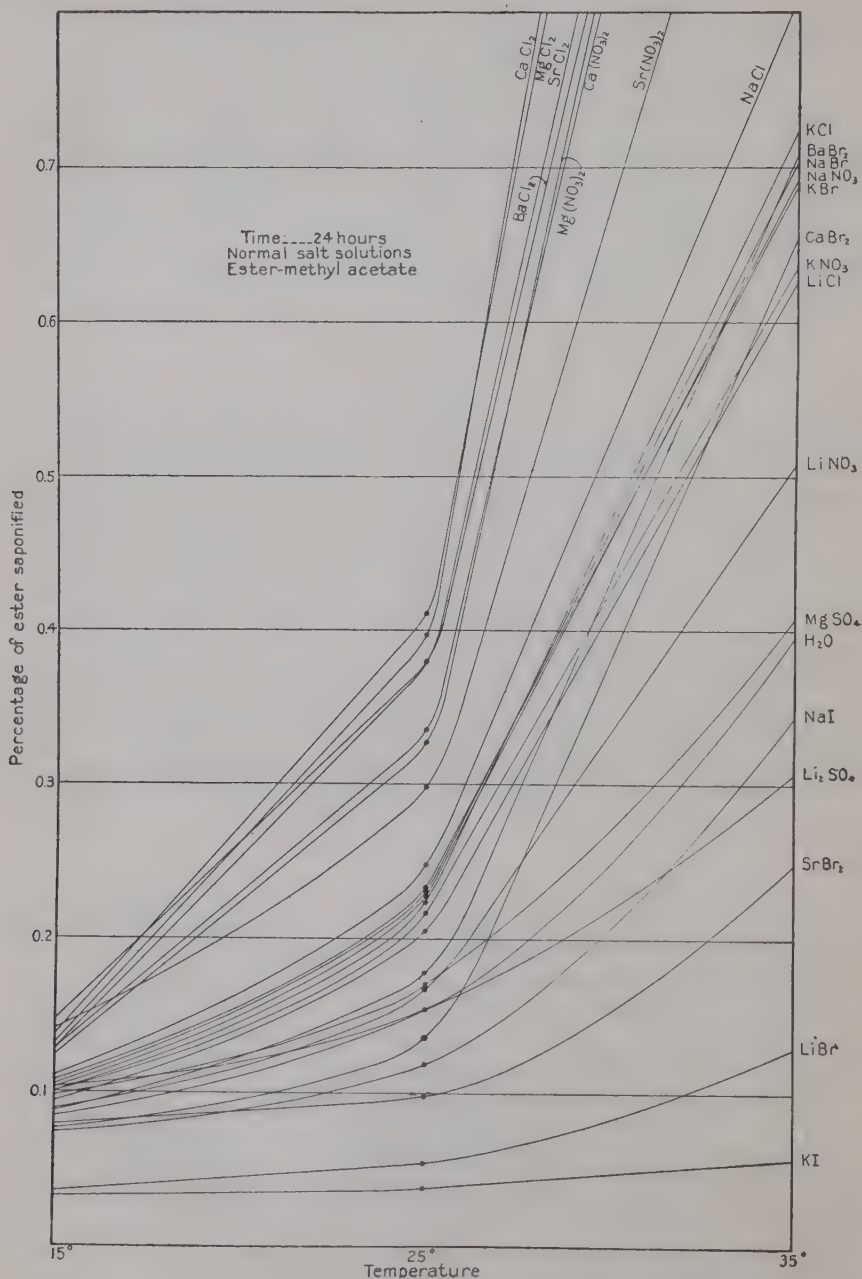


FIGURE 7.

The following curves show the amounts of methyl acetate saponified in 24 hours and in 48 hours.

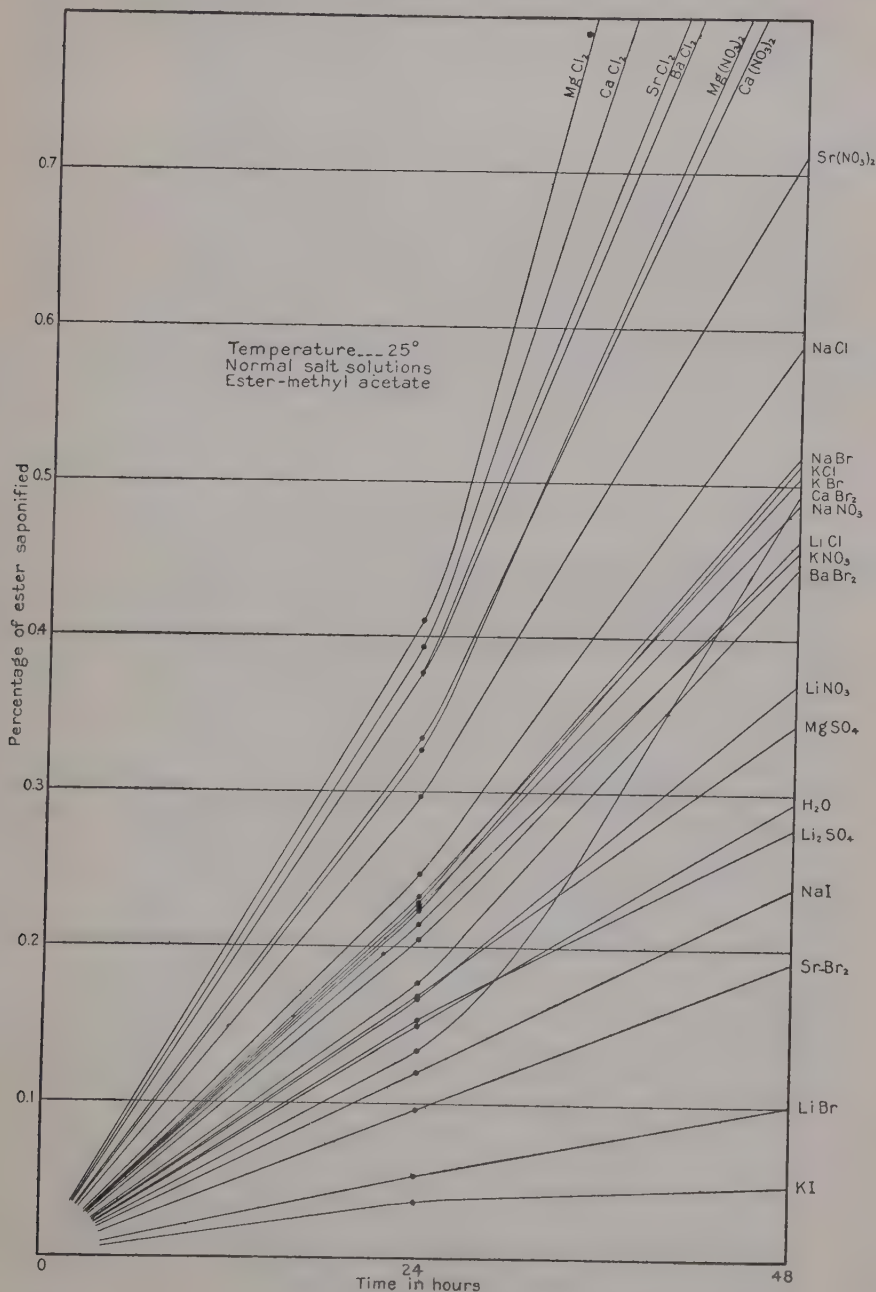


FIGURE 8.

The following curves show the percentages of methyl acetate saponified, using normal, half-normal, and quarter-normal solutions of salts.

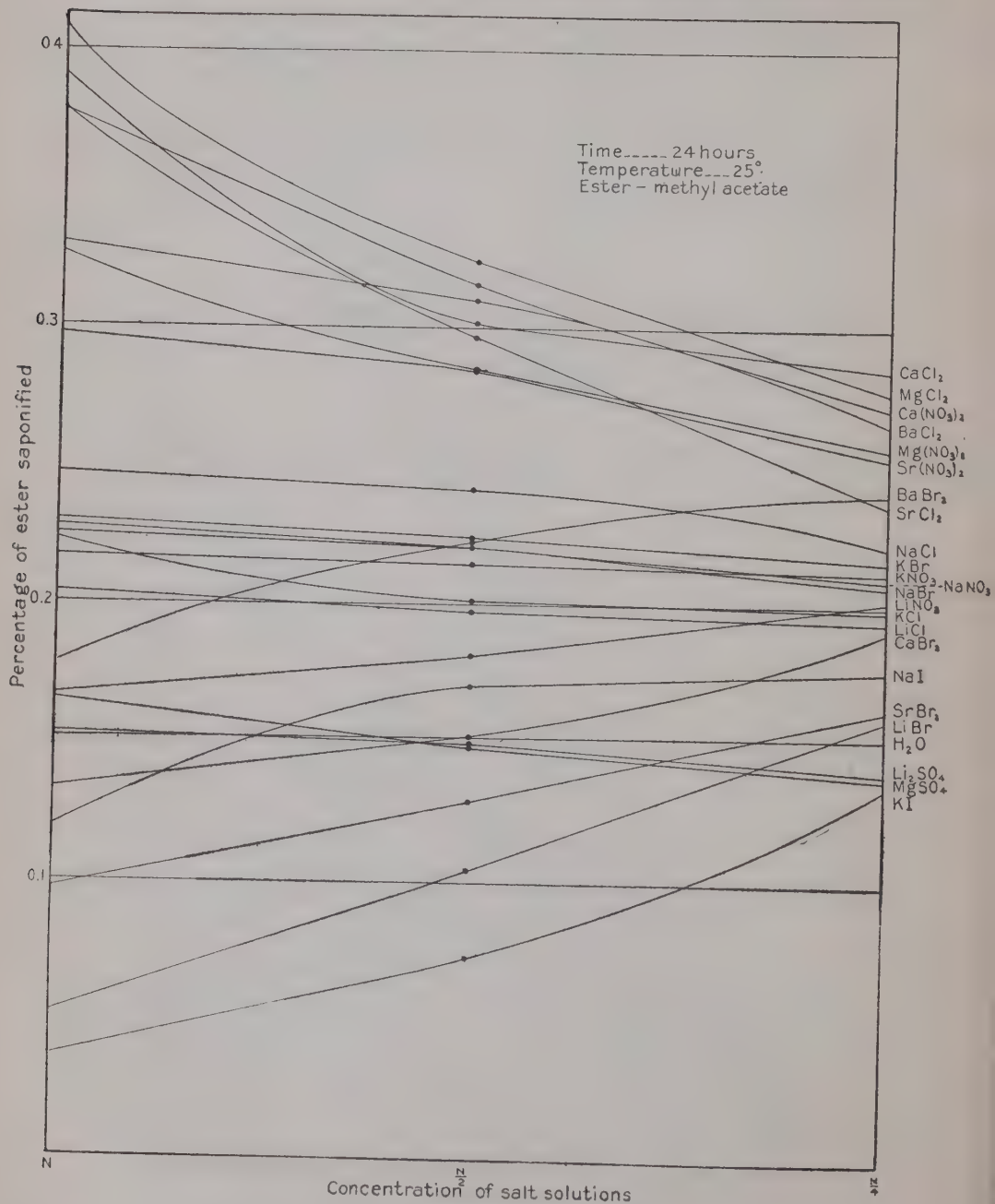


FIGURE 9.

The following curves show the amounts of methyl formate saponified at the two temperatures, 15° and 25°.

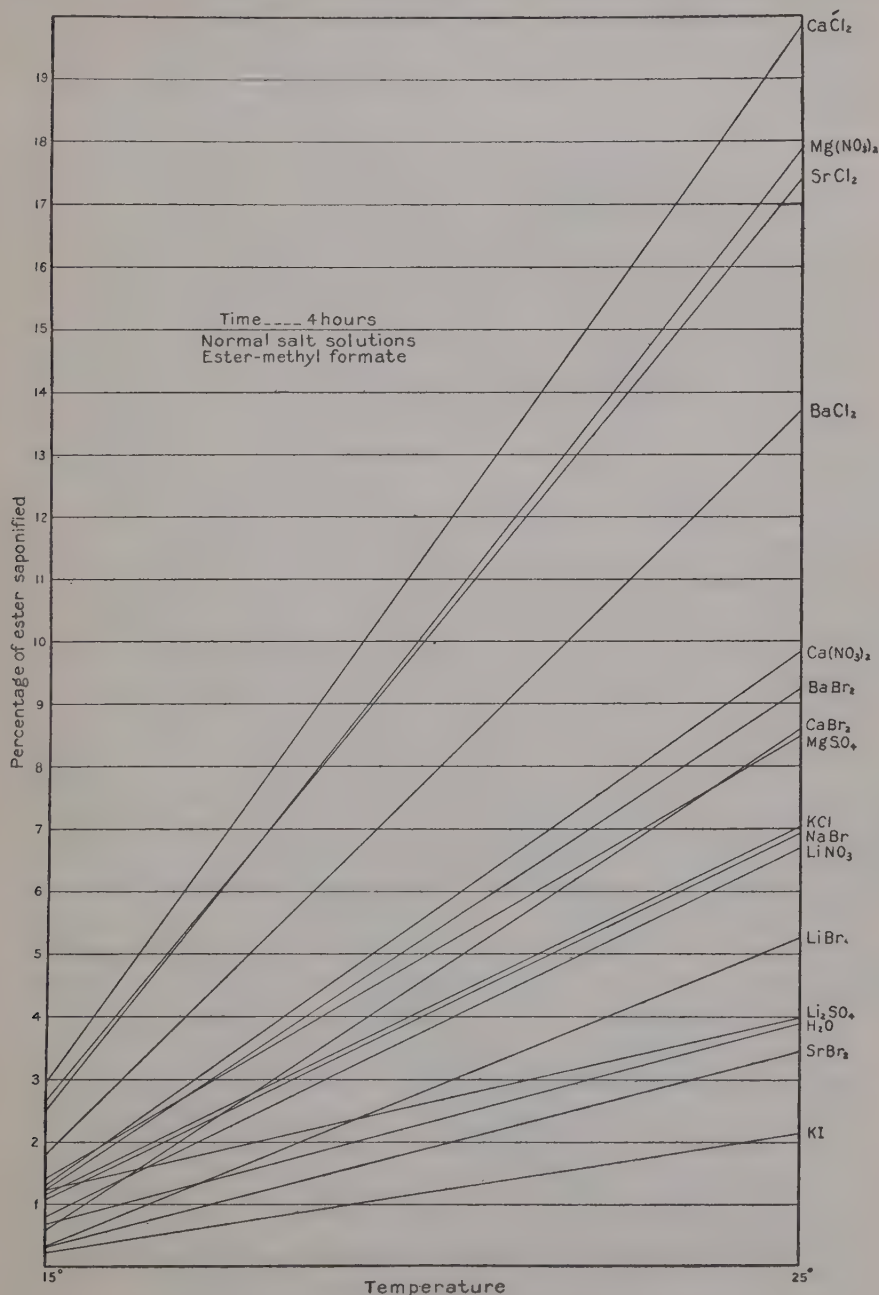


FIGURE 10.

The following curves show the percentages of methyl formate saponified in 4 and in 8 hours.

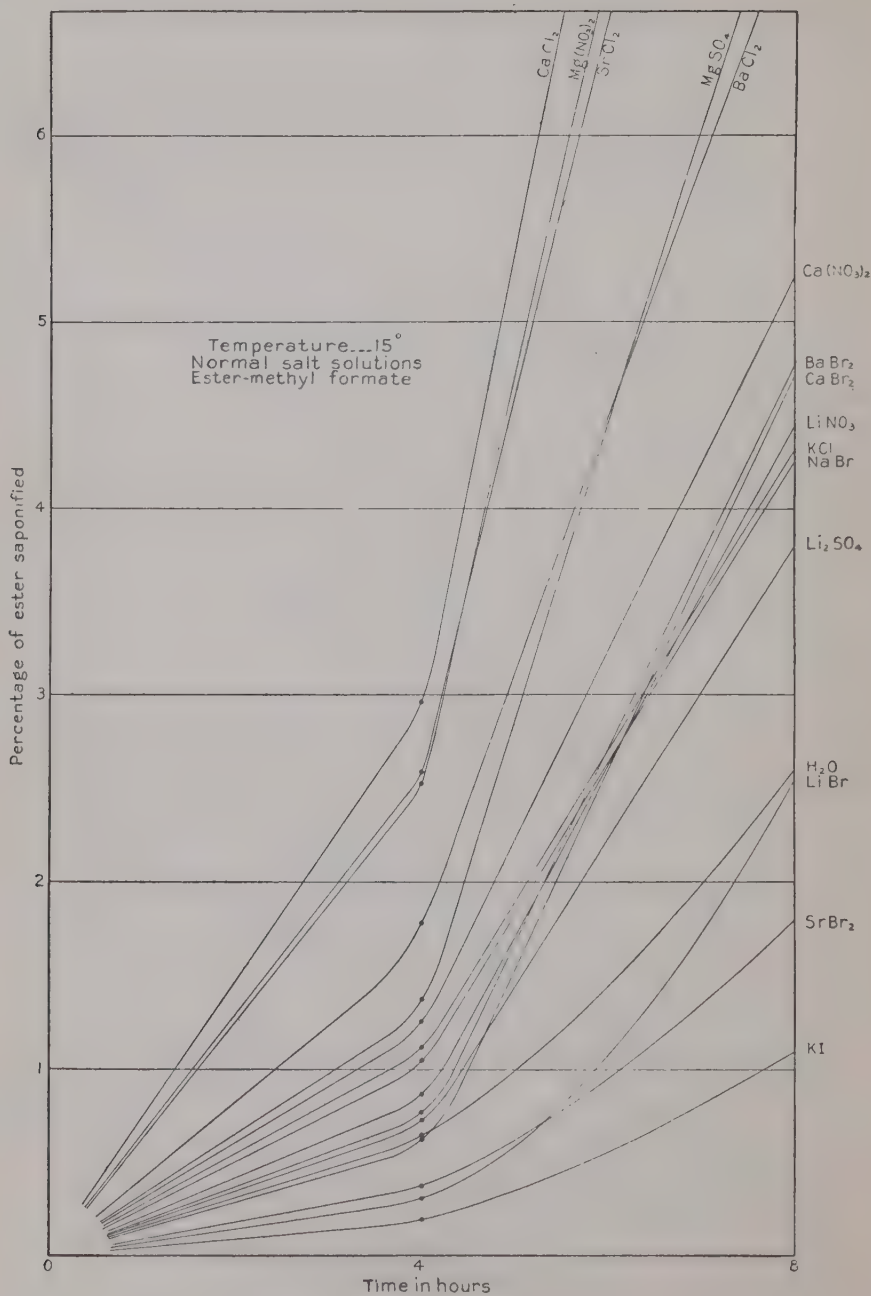


FIGURE 11.

The following curves show the percentages of methyl formate saponified with normal, half-normal, and quarter-normal solutions of salts.

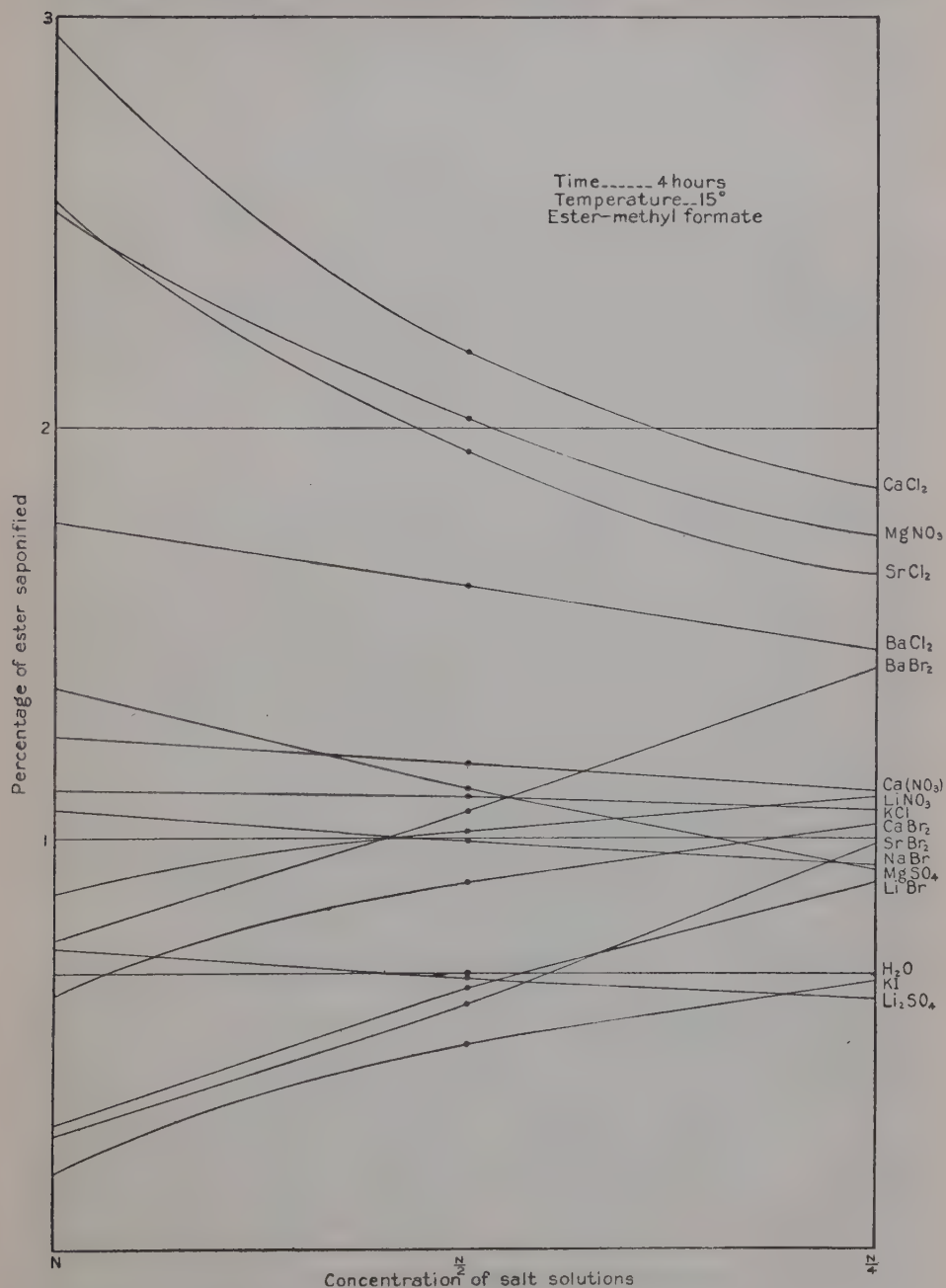


FIGURE 12.

TABLE 69.

No.	Solutions N.	15° 4 hrs.	25° 4 hrs.	15° 8 hrs.	Solutions N/2.	15° 4 hrs.	Solutions N/4.	15° 4 hrs.
1	{ 30 c.c. H ₂ O. }	0.670	3.89	2.60	{ 30 c.c. H ₂ O. }	0.661	{ 30 c.c. H ₂ O. }	0.680
2	{ 30 c.c. H ₂ O. }	0.667	3.91	2.58	{ 30 c.c. H ₂ O. }	0.667	{ 30 c.c. H ₂ O. }	0.680
3	{ 31.56 c.c. KI. }	0.192	2.14	1.09	{ 30.81 c.c. KI. }	0.494	{ 30.42 c.c. KI. }	0.667
4	{ 31.56 c.c. KI. }	0.188	2.14	1.08	{ 30.81 c.c. KI. }	0.501	{ 30.42 c.c. KI. }	0.668
5	{ 31.26 c.c. CaBr ₂ . }	0.618	8.59	4.73	{ 30.54 c.c. CaBr ₂ . }	0.982	{ 30.33 c.c. CaBr ₂ . }	1.03
6	{ 31.26 c.c. CaBr ₂ . }	0.618	8.61	4.71	{ 30.54 c.c. CaBr ₂ . }	0.984	{ 30.33 c.c. CaBr ₂ . }	1.05
7	{ 30.87 c.c. SrCl ₂ . }	2.55	17.44	10.69	{ 30.45 c.c. SrCl ₂ . }	1.98	{ 30.27 c.c. SrCl ₂ . }	1.64
8	{ 30.87 c.c. SrCl ₂ . }	2.56	17.42	10.71	{ 30.45 c.c. SrCl ₂ . }	1.98	{ 30.27 c.c. SrCl ₂ . }	1.63
9	{ 30.87 c.c. CaCl ₂ . }	2.97	19.86	12.74	{ 30.39 c.c. CaCl ₂ . }	2.18	{ 30.27 c.c. CaCl ₂ . }	1.85
10	{ 30.87 c.c. CaCl ₂ . }	2.97	19.84	12.76	{ 30.39 c.c. CaCl ₂ . }	2.19	{ 30.27 c.c. CaCl ₂ . }	1.84
11	{ 31.48 c.c. Mg(NO ₃) ₂ . }	2.52	17.92	11.31	{ 30.66 c.c. Mg(NO ₃) ₂ . }	2.02	{ 30.36 c.c. Mg(NO ₃) ₂ . }	1.75
12	{ 31.48 c.c. Mg(NO ₃) ₂ . }	2.54	17.94	11.33	{ 30.66 c.c. Mg(NO ₃) ₂ . }	2.01	{ 30.36 c.c. Mg(NO ₃) ₂ . }	1.74

DISCUSSION OF RESULTS.

From figures 7 and 8 the salts which produce the greatest increase in velocity, and which have the largest temperature coefficients, are magnesium chloride, calcium chloride, strontium chloride, barium chloride, magnesium nitrate, calcium nitrate, and strontium nitrate. All of these salts crystallize with water of crystallization, varying from six to two molecules each. Next come salts that do not have water of crystallization, as sodium chloride, sodium nitrate, potassium chloride, and potassium bromide. Along with these salts we have some that have water of crystallization, as sodium bromide, calcium bromide, lithium chloride, lithium bromide, lithium nitrate, and magnesium sulphate, which seem to be exceptions in the light of the action of the other salts that crystallize with water.

Still more inexplicable are the curves for lithium sulphate, sodium iodide, strontium bromide, lithium bromide, and potassium iodide, since these curves are below the curve for pure water.

Take figure 9. As the dilution is increased, salts such as magnesium chloride show a marked decrease in velocity; the salts with no water of crystallization show a less decrease, while the apparent exceptions, such as calcium bromide, strontium bromide, etc., show a marked increase in velocity, most of their curves ending above the curve for water.

Let us now consider the salts of any one metal (figures 7 and 8), *e. g.*, calcium. The chloride increases the velocity more than the nitrate, the nitrate more than the bromide. With potassium and sodium the chloride has more effect than the nitrate, the nitrate more than the bromide, the bromide more than the iodide. Of the salts studied, the sulphates have the least effect. There also seems to be a general relation between the metals themselves, as magnesium, calcium,

strontium, and barium, although in the series lithium, sodium, and potassium, lithium seems to be an exception.

The curves for the methyl formate are of the same general character, the only difference being that the curves are more extended, more being above the curve for water, probably due to the larger amount of saponification. The curves for calcium bromide, barium bromide, and magnesium sulphate with methyl formate do not appear to be exceptions, as they fall above the curves for salts with no water of crystallization.

Kellogg¹ found in the case of the halides of potassium that the chloride increased the reaction the most, the bromide less and the iodide least, normal potassium iodide actually decreasing the velocity. This apparently points to the fact that the anion plays an important part in the total effect of the salt on the reaction velocity. With more dilute solutions of potassium iodide (0.25 N) the velocity of the reaction is increased. Kellogg's curves for strontium chloride, calcium chloride, and barium chloride show that the cation must also be taken into account. A possible explanation of the behavior of barium bromide, calcium bromide, etc., may be that the total effect due to these salts is due to a combination between a cation tending to increase the velocity and an anion tending to decrease the velocity.

Kellogg¹ also finds that there is a concentration for each salt that will produce the greatest increase in the velocity of the reaction. Still further increase or decrease in the concentration from this point diminishes the velocity of the reaction.

The action of the apparent exceptions which manifested themselves in the study of this problem, *i. e.*, lithium nitrate, lithium bromide, calcium bromide, etc., may be due to the concentration of maximum saponification not having been reached, since these salts on dilution all increase the velocity. It is altogether probable that had the dilution been still farther increased, the apparent exceptions would have proved not to be exceptions at all. This seems to be all the more true, in that the curves of figure 10, where larger percentages of methyl formate are saponified, show that barium bromide, calcium bromide, and magnesium sulphate have greater effect than potassium chloride and sodium bromide. Therefore, it is more than probable that with solutions so dilute as to reach the dilution of maximum saponification, and with a larger amount of ester saponified, most of the apparent exceptions in figures 7 and 8 would no longer be exceptions, but we would have a general relation between salts with water of crystallization and salts without, the former increasing the velocity to a larger extent than the latter, having a larger temperature coefficient and decreasing more with dilution.

We are not satisfied with the results with strontium bromide, and hope in the near future to do more work with this salt.

¹Journ. Amer. Chem. Soc., **31**, 886 (1909); **35**, 396 (1913).

The position of the curve for a salt, then, seems to be a function of its water of crystallization supplemented by an effect due to the ions it forms, *e. g.*, water of crystallization would place the curve above the curves of salts that do not have water of crystallization; the anion $\bar{\text{Cl}}$ would place it above a salt with an anion $\bar{\text{NO}_3}$ or $\bar{\text{Br}}$; and the cation ^{++}Mg would place it above a salt with a cation ^{++}Ca , ^{++}Sr , or ^{++}Ba . This general relation appears to hold among the salts that have no water of crystallization. On figures 8 and 9 the lithium salts do not seem to fit in with the sodium and potassium salts, but what has been said about calcium bromide and barium bromide applies also to these salts, as is shown by figures 9, 10, and 11.

How can we explain this increase in the velocity of the reaction caused by salts that have water of crystallization, and the decrease in their effect on dilution.

Getman and Bassett¹ showed that the salts having water of crystallization are in solution the most hydrated. Assuming that the effect of the salts with water of crystallization is due to their being hydrated, let us see what we should expect.

(1) According to Getman and Bassett, the chlorides, nitrates, etc., of such salts as magnesium, calcium, strontium, and barium would increase the velocity of the reaction to very nearly the same extent, and this is much greater than with the non-hydrated salts.

(2) As the concentration decreases the effect would be lessened, since the total combined water would be less, the decrease being far more rapid than in the case of non-hydrated salts.

(3) From the work of Pearce,² who showed that the hydrating power of a cation is inversely proportional to its atomic volume, we should expect the curves for the salts of magnesium, calcium, barium, and strontium with a common anion, to be similar to those found by him, *i. e.*, magnesium salts have the greatest effect, then calcium, strontium, and barium.

Let us see if the experimental data confirm these conclusions, based on the assumption that between salts that have water of crystallization and salts that do not, the difference in action is due largely to the hydrates formed by the salts with water of crystallization.

Taking into consideration the facts brought out earlier, that the dilution of maximum saponification for the apparent exceptions had not been reached, and that larger percentages of ester saponified would also tend to make the apparent exceptions not real, we can draw from the curves the following conclusions:

(1) Salts with water of crystallization increase the velocity of the reaction much more than salts without water of crystallization.

¹Carnegie Inst. Wash. Pub. No. 60, 15 (1907).

²*Ibid.*, 180, 57 (1913).

(2) The effect of salts with water of crystallization decreases, on dilution, much more than the salts without water of crystallization.

(3) Among the metals with common anions, as magnesium, calcium, strontium, and barium chlorides or nitrates, the curves are arranged in the order of the decreasing atomic weights of the cations.

We therefore conclude that between salts with water of crystallization and salts without, on the saponification of esters, the difference in action is probably due to the chemical difference between hydrated and nonhydrated salts or between free and combined water. As an explanation of this difference in action we offer the suggestion that the combined water is more highly ionized than free water, and with hydrated salts we have this effect added to the salt effect shown in the case of nonhydrated salts.

Pearce¹ shows that the cations are the ones that are most strongly hydrated, the anions, if hydrated at all, being only slightly so.

The curves we find for the halides of potassium show that in the saponification of esters the anions play an important part. This is in line with what Kellogg² found. It therefore seems probable that the anions are also hydrated to a certain extent.

But how can the larger temperature coefficient of reaction velocity of the hydrated salts be accounted for, since with rise in temperature the hydrates become less complex? A study of figures 8 and 11 shows that, temperature being constant, the amounts of ester saponified in the presence of the hydrated salts, as the time increases, is much greater than the amounts saponified in the presence of the non-hydrated salts. This is probably due to the larger amount of acid formed by the saponification of the ester by combined water. With rise in temperature the larger amount of acid would give us a larger temperature coefficient. Another factor to be taken into consideration is the hydrolysis of the hydrated salts, which, though negligible at low temperature, increases greatly as the temperature rises. The increased fluidity of the solution must also be taken into account, the hydrates becoming less complex with rise in temperature. These three factors would probably offset the decomposition of the hydrates, giving less combined water, with the result that we should have a larger temperature coefficient of reaction velocity for the hydrated than for the non-hydrated salts.

From the standpoint of hydrates breaking down with rise in temperature, let us consider the effect of such rise on chemical reactions in general. The influence of temperature on the velocity of reactions is usually very great.

Berthelot³ showed that the velocity with which an ester is formed is about 22,000 times as great at 200° as at 7°.

¹Carnegie Inst. Wash. Pub. No. **180**, 57 (1913).

²Journ. Amer. Chem. Soc., **31**, 886 (1909); **35**, 396 (1909).

³Essai de Mécanique Chimique, **2**, 93 (1879).

Spohr¹ finds that cane sugar is inverted 5 times as rapidly at 55° as at 25°. Various attempts have been made to explain the effect of rise in temperature on the velocity of chemical reactions. A decrease in the viscosity of the medium with rise in temperature, allowing the ions to move more rapidly, a decrease in the mass of the ion with rise in temperature, and the increased kinetic energy of the molecules and ions, have been cited as the causes of the great increase, with rise in temperature, in reaction velocity. None of these theories seems sufficient to account for such an increase in the velocity of reactions as was noticed by Berthelot and others.

From the solvate theory of solution we see that ions and molecules attract to them molecules of the solvent. We should expect these ions to react more slowly, especially if the solvate were very complex, since the solvate would act as a protective covering around the ions and diminish the velocity with which they would react with one another. But suppose the temperature is raised; the solvate would become less and less complex, until finally the ions would not have any appreciable protective covering. In such a case, where the ions are in direct contact, we should expect the velocity of the reaction to be greatly increased.

We therefore offer this tentative suggestion as one of the most important causes of the increase in the velocity of chemical reactions with rise in temperature.

In conclusion, we can say that the chemical differences between free and combined water, brought out in the study of this problem, are strictly analogous to the physical differences between free and combined water, as shown by their power to absorb light, which led us to investigate this problem.

SUMMARY.

The following conclusions have either been confirmed or brought out in this investigation:

(1) The reaction involving the decomposition of an ester proceeds slowly at ordinary temperatures, and therefore can be readily and accurately studied.

(2) The hydrolysis of the chlorides and nitrates, etc., of calcium, magnesium, strontium, and barium employed in the study of this problem is so small that it can not account for the differences observed.

(3) Salts with water of crystallization increase the velocity of the saponification of an ester to a greater extent than salts with no water of crystallization.

(4) On dilution, the effect with salts having water of crystallization decreases more rapidly than with salts without crystal water.

¹Zeit. phys. Chem., **2**, 195 (1888).

(5) The curves for the saponification of methyl formate are very similar to those for methyl acetate.

(6) The large effect of salts with water of crystallization is probably due, in part, to their being hydrated, combined water being more highly ionized than free water.

(7) The amount of the saponification (and therefore the position of the curve) seems to be due to the combined effect of both cation and anion.

(8) It is probable that anions as well as cations are hydrated.

(9) The hydration of cations is inversely proportional to their atomic volumes.

(10) There seems to be a dilution of maximum saponification for each salt.

(11) Hydrated salts show a large temperature coefficient, notwithstanding the decomposition of hydrates with rise in temperature.

(12) Decomposition of hydrates may play an important rôle in the increased velocity of chemical reactions with rise in temperature.

(13) The chemical differences between free and combined water are analogous to the physical differences.

CHAPTER VI.

EFFECT OF NEUTRAL SALTS ON THE HYDRATION OF ACETIC ANHYDRIDE.

BY GERALD C. CONNOLLY.

HYDRATION OF ACETIC ANHYDRIDE.

The hydration of acetic anhydride has been studied by several investigators with varying degrees of success.

Menschutkin and Vasilieff,¹ in studying the decomposition of acetic anhydride by water, attempted to find a constant for the velocity of hydration. They did not succeed because the two substances did not mix in all proportions, and no solvent could be found that did not act either on the substances themselves or on the products of the reaction. They studied the change in a homogeneous mixture of acetic acid, acetic anhydride, and water, and found that the reaction was not as rapid as had generally been supposed.

Hinsberg² showed that the acetic anhydride was soluble in the water *in the anhydride state*, and that the presence of water was not an obstacle to the employment of the anhydride as such.

A. and L. Lumière and H. Barbier³ showed that a solution of acetic anhydride in water possesses practically all the properties of acetic anhydride and was sufficiently stable for acetylation purposes.

In a second paper⁴ A. and L. Lumière and H. Barbier stated that 12 per cent acetic anhydride was soluble in water, solution taking place immediately on shaking. They prepared 5 and 10 per cent solutions of acetic anhydride in cold water and set them aside. From these solutions equal aliquot parts were withdrawn every 10 minutes and added to a slight excess of aniline, the excess being known. Reaction took place quantitatively between the aniline and the acetic anhydride not hydrated by the water, forming acetanilide and an equivalent of acetic acid. The total acid present was then determined by titration with a normal solution of sodium hydroxide in the presence of phenolphthalein. They found that the rate of hydrations was at first rapid and then decreased, the rate being more rapid the greater the initial dilution of the anhydride and the higher the temperature. They carried out two experiments at 0° and two at 15°. They also prepared alcoholic solutions of the anhydride and showed that when molecular proportions were used, esterification was incomplete, even after a month.

Benrath,⁵ by means of change in density, attempted to measure the rate at which the anhydride combined with the water in a solution of

¹Journ. Russ. Phys. Chem. Soc., **21**, 192 (1889).

²Ber. d. deutsch. chem. Gesell., **23**, 2962 (1890).

³Bull. Soc. Chim., **3**, 33, 783 (1905).

⁴*Ibid.*, **3**, 35, 625 (1906).

⁵Zeit. phys. Chem., **67**, 501 (1909).

acetic acid. He concluded that, with equivalent quantities of anhydride and water, the reaction was mono-molecular.

Rivett and Sidgwick,¹ using dilute aqueous solutions, followed the hydration by measuring the electrical conductivity. The measurements were made at 25°. The velocity of hydration showed that the reaction was mono-molecular and was not catalyzed by hydrogen ions; and that beyond a certain point the constant decreases steadily with increasing concentration.

Orton and M. Jones² concluded that the hydration of acetic anhydride in acetic acid as a solvent is a slow reaction of the second order; that on dilution the increase in velocity was approximately proportional to the amount of water present, and that the relation of the velocity factor to the temperature was normal. The effect of catalysts was also studied. It was found that acids were powerful catalysts of the hydration. The effect was most obvious in media containing but little water, diminishing as the proportion of the water increased, being least obvious in pure water. The value of the velocity factor was a linear function of the concentration of the acid. Alkalies and hydrolyzed salts were also found to act as powerful catalysts to the hydration in aqueous solutions.

Philip³ made a study of the reaction between acetic anhydride and water in glacial acetic acid, by determining the freezing-points of the mixture taken at frequent intervals.

Wilson and Sidgwick⁴ studied the rate of hydration of a number of acid anhydrides. The rate of formation of the acid was determined by measuring the increase in the electrical conductivity of a solution of the anhydride in water.

NEUTRAL SALT ACTION.

There has been but little experimental work done on the problem of the effect of the neutral salt on the hydrolysis by water alone. Most of the work has had to do with the effect exerted by a neutral salt on the activity of an acid used to catalyze the reaction. This latter is what we generally understand by the term "neutral salt action." It has been studied mainly in two reactions: (1) the rate of inversion of cane sugar in the presence of acids, and (2) the catalytic hydrolysis of esters. In general it has been found that neutral salt action is not greatly influenced by temperature, and that the influence of neutral salts is regarded as independent of the acid employed as catalyst.

Practically the only work done on the effect of neutral salts on hydration alone is that due to Kellogg, published in a series of three articles.⁵ He showed that the rate of hydrolysis of ethyl acetate by water is

¹Journ. Chem. Soc., **97**, 733, 1677 (1910).

²*Ibid.*, **101**, 1708 (1912).

³Proc. Chem. Soc., **28**, 259.

⁴Journ. Chem. Soc., **103**, 1959 (1913).

⁵*Ibid.*, **31**, 403 (1909); 886 (1909); **35**, 396 (1913).

greatly accelerated by potassium chloride, bromide, and iodide; also by the chlorides of sodium, lithium, calcium, strontium, barium, and cadmium. The reaction was studied at 100°. Results show that the accelerating effect of lithium chloride is greater than that of sodium chloride, although the degree of ionization is less, and that the chlorides of calcium, barium, and strontium have a greater effect than either sodium or potassium chloride, although they are less ionized. Cadmium chloride, the least ionized of all the chlorides studied, produced the greatest effect. Kellogg concluded that the effect produced by a neutral salt on the hydrolysis of ethyl acetate, is due to a specific influence on the non-ionized portion of the salt rather than to any function of the ions.

STATEMENT OF THE PROBLEM.

Jones and Anderson¹ found that the absorption spectra of salts like neodymium chloride and nitrate, when dissolved in non-absorbing solvents such as water and alcohol, depended largely on the nature of the solvent in which the salt was dissolved; *e. g.*, neodymium chloride dissolved in water had a different absorption spectra from that of neodymium chloride dissolved in methyl or ethyl alcohol. They found for the first time what they called "solvent" bands, showing that the dissolved substance was combined with more or less of the solvent, forming in the one case "hydrates" and in the other "alcoholates." Alcoholates had, as would be expected, very different resonance from hydrates.

Jones and Strong² extended the work of Jones and Anderson to a large number of solvents and to a fairly large number of non-absorbing salts, and showed that these solvents had a marked influence on the absorption spectra shown by salts dissolved in them. They were able to distinguish between the spectra of salts dissolved in normal alcohol and those in the isomeric alcohol. It would lead us too far here to discuss this work in detail; therefore, reference only can be made to the original papers.

Jones and Guy³ built the most sensitive radiomicrometer constructed up to that time, and by means of it they studied quantitatively the intensities of absorption lines and bands. They found that, while solutions of slightly hydrated salts were about equally transparent with pure water, *solutions of strongly hydrated salts were very much more transparent than pure water.*

The work of Jones and Guy was repeated by Jones, Shaeffer, and Paulus,⁴ using an even more sensitive radiomicrometer constructed by Shaeffer, and confirmed conclusions reached by Jones and Guy. They found solutions of strongly hydrated salts which were as much as *40 per cent more transparent than a depth of pure water equal to the water*

¹Carnegie Inst. Wash. Pub. No. 110 (1909).

²*Ibid.*, 130 (1910) and 160 (1911).

³*Ibid.*, 190 (1913).

⁴*Ibid.*, 210 (1915).

in the solution in question. This showed that water of hydration has a very different resonance from that of pure water.

Having found this *physical difference* between combined and free water, the problem was now to see if there was *any chemical difference*.

Jones and Holmes¹ studied the action of strongly hydrated salts and slightly hydrated salts on the saponification of methyl acetate and of methyl formate in the following manner: He measured the velocity of saponification of the ester by pure water, by a solution of slightly hydrated salts containing the same amount of water as the pure water used, and by solutions of strongly hydrated salts containing the same amount of water as the free water employed, and as the water in the slightly hydrated salts. Taking into account the hydrolysis of the strongly hydrated salts he found that these salts saponified much more rapidly than pure water itself.

The reaction studied by Jones and Holmes was a very slow one and indicated that combined water has greater activity than free water. We wished to investigate the same problem, using a reaction that proceeded much more rapidly; therefore we chose the reaction involving the conversion of acetic anhydride into acetic acid.

EXPERIMENTAL.

PURIFICATION OF MATERIAL.

Very pure acetic anhydride was necessary for our work. The physical properties as described varied greatly. The boiling-points given ranged anywhere from 135° to 140°, at 760 mm. pressure. The densities given varied between 1.07 and 1.09. From this it can be seen that it was impossible to test its purity by the ordinary simple means. Acetic acid is the impurity most likely to be present in the anhydride, and is very difficult to detect if only small amounts are present; 0.51 gram of pure acetic anhydride, when completely hydrated, is equivalent to 100 c.c. N/10 solution of sodium hydroxide; while the same weight of a mixture containing 1 per cent of acetic acid is equivalent to 99.85 c.c. This is within the experimental error. The method finally used to purify the anhydride was to distill repeatedly, using a five-bulb distilling head, discarding the first and last fractions. This gave a very pure anhydride with a constant boiling-point.

The salts used in this work were the purest obtainable. They were repeatedly recrystallized.

APPARATUS AND SOLUTIONS.

All of the glassware used was of Jena make. The constant temperature baths were those commonly used in this laboratory. All solutions were made up gravimetrically, except those of the non-hydrated salts

¹See Chapter V.

which were weighed directly. The solution of sodium hydroxide used in titration was made up approximately half-normal, from sodium hydroxide from alcohol. It was preserved in an apparatus protected from impurities in the air. It was standardized by titrating against a standard solution of sulphuric acid of about the same strength. The purest water obtainable was always used.

MANIPULATION.

The method in principle is a modification of that of Menshutkin and Vasilieff, and later employed by A. and L. Lumière and Barbier. In order that the results should be comparable, the amount of water present must be kept constant and the specific gravity of the salt solution was therefore first taken; this gave the weight of 1 c.c. From analysis, that part of the weight due to the anhydrous salt alone was known for each cubic centimeter. This known weight of salt, subtracted from the weight of 1 c.c. of solution, gave the weight due to the pure water alone. This, divided into the weight of 1 c.c. of pure water at that temperature, gave the amount of solution in cubic centimeters equivalent to 1 c.c. of pure water. The amount of solution thus calculated was pipetted into a 250 c.c. Jena bottle. An equivalent of 100 c.c. of pure water was taken in all determinations. The bottle was suspended in the constant-temperature bath. There was also placed in the bath a bottle containing the anhydride and a number of small empty bottles of 50 c.c. capacity.

When all had come to the temperature of the bath, the bottle was removed and 5 c.c. of the anhydride introduced. Time was reckoned from when the anhydride was first added. Solution took place immediately on shaking, except in the case of the very concentrated solutions. Equal aliquot portions were removed and placed in the small 50 c.c. bottles, the whole being kept in the bath. These small bottles were removed, first every 5, then every 10 minutes, and a slight known excess of aniline added. This, on shaking, combines with the residual acetic anhydride, precipitating acetanilide and liberating an equivalent of acetic acid.

The total amount of acetic acid was then titrated directly in the bottle, using the half-normal solution of sodium hydroxide in the presence of phenolphthalein as indicator. Corallin had been tried, but phenolphthalein was more satisfactory. The amount of acetic acid due to the water alone was then calculated, using the simple formula $y = 2z - x$, where y is the amount of acetic acid due to the water alone, z is the total amount of acetic acid as measured on the burette, and x is the total amount of acetic acid that can be formed if all the acetic anhydride has been completely hydrated.

Two temperatures, 15° and 25°, were employed. Only one concentration of acetic anhydride was used (approximately 5 per cent),

because if two were employed the results would not then be comparable on account of volume changes. For the salts molar m , half-molar $\frac{m}{2}$, and quarter-molar $\frac{m}{4}$ solutions were taken in all cases, and usually another solution as concentrated as possible. The time is expressed in minutes and all the results in percentages.

TABLE 70.—Potassium chloride.

Time.	Concentration (temperature, 15°).						Concentration (temperature, 25°).					
	H ₂ O.	3 M.	2 M.	M.	M/2.	M/4.	H ₂ O.	3 M.	2 M.	M.	M/2.	M/4.
<i>min.</i>												
5	32.86	15.4	22.4	30.00	32.22	33.10	43.77	25.36	28.70	41.43	42.56	43.54
10	57.69	30.8	39.5	52.15	54.97	56.72	71.93	46.60	56.26	65.57	69.47	71.34
20	79.95	50.2	60.4	75.22	77.79	80.31	93.06	72.20	85.78	89.07	91.59	92.84
30	90.15	64.1	73.9	86.52	88.53	90.89	98.65	86.36	92.66	96.15	97.53	98.90
40	95.17	74.1	83.4	92.09	94.16	95.54	99.91	93.64	96.64	98.10	99.00	99.59
50	97.44	81.98	89.5	95.16	96.72	97.32						
60	98.34	86.8	92.6	97.58	98.02	98.53						

TABLE 71.—Calcium chloride.

Time.	Concentration (temperature, 15°).					Concentration (temperature, 25°).				
	H ₂ O.	4 M.	M.	M/2.	M/4.	H ₂ O.	4 M.	M.	M/2.	M/4.
<i>min.</i>										
5	32.86	2.55	32.54	32.92	32.88	43.77	20.53	50.18	50.49	49.99
10	57.69	15.60	56.88	57.71	57.24	71.93	50.25	69.46	72.81	73.45
20	79.95	41.80	80.70	80.97	81.06	93.06	78.65	97.32	95.56	95.92
30	90.15	58.65	91.87	91.86	91.96	98.65	92.74	100.00	97.66	99.36
40	95.17	70.55	96.65	96.39	96.82	99.91	96.70		100.00	100.00
50	97.44	78.85	98.72	98.35	98.34					
60	98.34	85.06	99.84	99.07	98.59					

TABLE 72.—Magnesium Chloride.

Time.	Concentration (temperature, 15°).						Concentration (temperature, 25°).					
	H ₂ O.	4 M.	2 M.	M.	M/2.	M/4.	H ₂ O.	4 M.	2 M.	M.	M/2.	M/4.
<i>min.</i>												
5	32.86	0.97	20.30	30.80	31.30	32.82	43.77	1.85	29.70	40.00	41.60	43.09
10	57.69	13.50	37.45	48.30	51.05	55.58	71.93	25.05	56.51	69.41	70.59	71.98
20	79.95	24.12	59.11	74.82	77.96	80.60	93.06	72.25	80.26	89.79	92.39	93.31
30	90.15	50.50	74.02	87.39	89.88	90.76	98.65	93.21	92.37	96.06	97.00	97.89
40	95.17	67.45	82.68	92.25	93.74	95.89	99.91	96.53	97.46	98.45	98.84	98.88
50	97.44	84.00	88.87	96.42	97.20	98.13						
60	98.34	88.26	92.64	97.26	98.14	98.60						

DISCUSSION.

There is one difficulty in the study of this problem that must first be pointed out, *i. e.*, the necessary use of a strong alkali (half-normal solution of sodium hydroxide) with which to titrate the acetic acid formed. This necessarily introduces some error, since a difference of 0.1 c.c. in reading the burette would make a difference of over 1 per cent. A more dilute solution of an alkali could not be used, since too large a quantity of such a solution would be required.

The rate of the decomposition of the anhydride is at first very rapid, then gradually decreases as the hydration approaches completion. In this respect the reaction differs from similar ones studied, such as the hydrolysis of esters, since in these cases the reactions are reversible. There is also a marked increase in the rate of decomposition of the anhydride with rise in temperature.

The values obtained for the salt solutions, having a fixed quantity of water, are compared with those obtained with pure water. All of the very concentrated salt solutions show a marked decrease in the rate of decomposition of the anhydride. This retardation is greater with the two hydrated salts used than with the non-hydrated salt. However, with the more dilute solutions, molar, etc., this is not the case. Magnesium chloride and potassium chloride hinder the rate of decomposition to about the same extent, this being slightly greater with the solutions of magnesium chloride. Calcium chloride, on the other hand, shows a slightly accelerating action.

CONCLUSION.

These relations are interesting, but as yet no general or final conclusions can be drawn. The problem is to be investigated farther, using a much larger number of salts, both hydrated and non-hydrated.

CHAPTER VII.

CONDUCTIVITY OF CERTAIN ORGANIC ACIDS IN ETHYL ALCOHOL.

BY H. H. LLOYD AND JOHN B. WIESEL.

During the past six years a fairly thorough and systematic study of the conductivity and dissociation of aqueous solutions of organic acids, as affected by temperature and by dilution, has been in progress in this laboratory.¹ Very little work had been done upon solutions of organic acids in absolute ethyl alcohol (as will become evident from the historical review that follows), and it was therefore decided to extend our investigations into this field.² Accordingly, Wightman, Wiesel, and Jones undertook a preliminary investigation of the problem, worked out a fairly satisfactory method of procedure, and made conductivity measurements of nine organic acids.³ The present investigation is a continuation and extension of their work.

HISTORICAL SKETCH.

The property of water, which, in the pure condition, conducts electricity only very slightly, to become conducting upon the addition of many compounds which of themselves are non-conducting, was known to De la Rive, and was the subject of interesting experiments by Faraday; and the fact that solvents other than water exhibit the same phenomenon (of acquiring conductivity upon the addition of non-electrolytes) has been studied by a large number of workers;⁴ but to Kohlrausch and Ostwald belongs the credit of having placed investigations in this field once and for all upon a firm scientific basis.

The contributions of Kohlrausch may be briefly described as follows: (1) The development of a convenient and precise method for measuring conductivity;⁵ (2) the emphasis on and the determination of the extent to which conductivity is influenced by temperature; (3) the reduction of conductivity measurements to definite, fixed units; (4) the reference of conductivity not to weight per cent, as had been previously done, but to molecular volumes of solutions; that is, volumes which contain equivalent amounts of the dissolved substances;⁶ (5) the enunciation of the law of the independent migration velocities of ions.

Ostwald made the conductivity method of Kohlrausch more complete and more practicable by reducing the apparatus and the manipu-

¹Carnegie Inst. Wash. Pub. No. **170**, Part II (1912); No. **210**, Chap. II (1915).

²Amer. Chem. Journ., **44**, 156 (1910); **46**, 56 (1911); **48**, 320, 411 (1912); **50**, 1 (1913).

³Journ. Amer. Chem. Soc., **36**, 2243 (1914). Carnegie Inst. Wash. Pub. No. **210**, Chap. III (1915).

⁴Walden: Zeit. phys. Chem., **8**, 433 ff. (1891); **46**, 103 ff. (1903).

⁵Pogg. Ann., **138**, 379 (1869); **159**, 233 (1876); Wied. Ann., **11**, 653 (1880); **26**, 161 (1885).

⁶Wied. Ann., **6**, 145 (1879).

lation to the simplest possible terms.¹ He also showed how the law of independent migration velocities of ions could be used to calculate the μ_{∞} values of organic acids from those of their sodium salts.² In addition, just after Arrhenius on the basis of his dissociation theory, had pointed out³ the necessity of the parallelism between the strengths of acids and their conductivities, it was Ostwald who, led to similar ideas by other considerations, succeeded in demonstrating⁴ the existence of such a relation and thereby made the first contribution to the application and significance of conductivity in questions of chemical affinity. Further, from thermodynamical considerations, Ostwald derived his "dilution law,"⁵ which permits the calculation (from the molecular conductivities of any weakly dissociated substance at different dilutions) of its affinity constant, which is independent of the degree of dilution and is conditioned only by the nature of the dissolved substance. During his classical investigations in this field⁶ Ostwald determined the affinity constants of over 240 organic acids, and on the basis of these values drew many conclusions as to the composition and constitution of acids, thereby furnishing organic chemistry with a new and useful means of investigating questions of constitution.⁷

In a word, whereas Kohlrausch made the determination of conductivity possible, by developing a convenient and accurate method of measuring it, Ostwald pointed out the practical importance of these measurements by indicating their bearing upon the solution of other chemical problems.

The first serious attempt to study the conductivity of alcoholic solutions of organic acids was made in 1888 by Hartwig.⁷ This investigator employed the Kohlrausch method of measuring conductivity, and worked with solutions of formic, acetic, and butyric acids of varying concentrations, at temperatures ranging from 0° to 30°. He found that conductivity increased with rise in temperature, and calculated the temperature coefficients of conductivity by means of the equation

$$k_t = k_o (1 + at + \beta t^2)$$

No other conclusions, however, can be drawn from Hartwig's work, because he expressed his results in terms of grams of acid in 100 grams of solution instead of in terms of molecular concentrations.

In 1889 Kablukoff⁸ determined the conductivity of hydrochloric-acid gas in absolute alcohol and in alcohol-water mixtures at 25°. He found the molecular conductivity in pure alcohol to be about one-sixteenth of that in pure water. In the mixed solvent the conductivity increases

¹Zeit. phys. Chem., **2**, 561 (1888).

²*Ibid.*, **2**, 270 (1888); **3**, 170 (1889). Amer. Chem. Journ., **46**, 66 (1911).

³Bih. t. k. Ak., 1884.

⁴Journ. prakt. Chem., **30**, 93 (1884).

⁵Zeit. phys. Chem., **2**, 36, 270 (1888).

⁶*Ibid.*, **3**, 170, 241, 369 (1889).

⁷Wied. Ann., **2**, 33, 53 (1888).

⁸Zeit. phys. Chem., **4**, 429 (1889).

with increasing percentage of water, very slowly up to about 12 per cent of water (by weight), and then more rapidly. In every case the molecular conductivity increases slowly with dilution.

Wakeman¹ measured the conductivity of several organic acids and their sodium salts (as well as of hydrochloric acid, potassium iodide, potassium chloride, and sodium chloride) in alcohol-water mixtures ranging from pure water to 50 per cent alcohol. Using Lenz's values² for the relative migration velocities of the potassium and iodine ions in solutions of potassium iodide, he was able, by means of his conductivity measurements, to calculate the relative migration velocities of the chlorine, hydrogen, and sodium ions in the various mixed solvents which he employed. He then had all the data necessary to apply Ostwald's method³ for the determination of the μ_{∞} values of the organic acids from those of their sodium salts. From these values it was a simple matter to calculate percentage dissociation, and, thence, by means of Ostwald's dilution law, affinity constants.

The results obtained show that, for a given acid at a given dilution, increase in the percentage of alcohol causes a slight decrease in dissociation and a more rapid decrease in the affinity constant (k). For a definite alcohol-water mixture, the value of k decreases regularly with dilution, which seems to point to the action of an unknown influence which decreases the dissociation to such an extent that the formula $\frac{a^2}{(1-a)v}$ no longer holds. A very interesting feature of Wakeman's work is his attempt to extrapolate the value of molecular conductivity beyond 50 per cent alcohol, in the direction of 100 per cent alcohol; and he postulates that the conductivity approaches zero as a limit.

Schall⁴ determined the conductivity of oxalic, picric, and dichloroacetic acids in alcohol and in alcohol-water mixtures. The molecular conductivity of these acids in water is approximately the same, but Schall found that replacement of the water by alcohol decreases the conductivity to quite different extents. This he attributes chiefly to change in the degree of dissociation. In alcohol-water mixtures the acids were found to behave very differently from what they did in the pure solvents. Some appear to behave just the opposite of what might be expected; for example, picric acid gives a much higher, and each of the other acids a much lower conductivity value in water-alcohol mixtures than in pure alcohol.

In the meantime the conductivity method had been applied to solutions of electrolytes in a variety of non-aqueous solvents, with the result that not a single case was on record in which the Ostwald dilution law could be said to apply, even approximately. In order to test the

¹Zeit. phys. Chem., **11**, 49 (1893).

²Mem. de l'Acad. de St. Petersb., VII series, **30**, 9 (1882).

³Zeit. phys. Chem., **2**, 270 (1888); **3**, 170 (1889). See also Amer. Chem. Journ., **46**, 66 (1911).

⁴Zeit. phys. Chem., **14**, 701 (1894).

validity of this law for alcoholic solutions, Wildermann, in 1894, carried out an investigation¹ on the conductivity of certain organic acids (acetic, monochloracetic, dichloracetic, trichloracetic, and succinic) in absolute alcohol at 18°. Absolute alcohol was obtained free from aldehyde by treatment with silver nitrate, and from water by heating with lime. Great care was exercised in protecting it from the air, and a special apparatus was constructed, with the aid of which a measured quantity could be drawn out of the supply bottle directly into the conductivity cells. Because of the small values of the conductivities to be measured, the cells were constructed so as to have small constants; but in spite of this the external resistances required were high, and hence a graphite resistance rheostat was employed to make the tone minima more distinct. Before using, the cells were washed with running water for from 8 to 10 days. They could not be dried in the ordinary way by washing with alcohol and then evaporating the alcohol, because it was found that the alcohol which was in contact with the platinized electrodes was to some extent oxidized by the air to acetic acid. Therefore, after being washed with water, the cells were allowed to drain completely, after which alcohol was introduced so as to wash the glass walls without coming in contact with the electrodes, and then the alcohol was allowed to cover the electrodes. Some of the alcohol was then drawn off and fresh alcohol added, keeping the electrodes continuously covered, and this process repeated until the conductivity remained constant. This often cost a half day of work and from 300 to 500 c.c. of good absolute alcohol. All the solutions were made up in the cell, the most concentrated by introducing approximately the desired quantity of acid, and from this the others by repeated replacement of a portion of the solution with fresh alcohol. The strength of each solution was determined by titration of the portion removed.

Wildermann found that the conductivity of acetic, monochloracetic, and succinic acids was so small that the values were unreliable, and he was content to make the qualitative statement that between the volumes 10 and 160 these substances have a molecular conductivity which increases almost directly proportional to the volume.

In order to understand fully his conclusions in regard to the stronger acids, it will be necessary to consider briefly a few mathematical relations which Wildermann deduced from the dilution law of Ostwald.

As Ostwald showed, the dilution law

$$\frac{\mu_{\infty}(\mu_{\infty} - \mu_v)v}{\mu_v^2} = k \quad (\text{I})$$

for weakly dissociated compounds, takes the form

$$\mu_v^2 = vk_1 \quad (\text{II})$$

¹Zeit. phys. Chem., **14**, 231 (1894).

Assuming that a given acid in alcoholic solution obeys the dilution law, if we increase the volume from v to v_1 , we have, instead of (I) and (II)

$$\frac{\mu_{\infty}(\mu_{\infty} - \mu_{v1})}{\mu_{v1}^2} v_1 = k \quad (\text{I}')$$

and

$$\mu_{v1}^2 = v_1 k^{(1)} \quad (\text{II}')$$

Combining (II) and (II') we get

$$\frac{\mu_{v1}^2}{\mu_v^2} = \frac{v_1}{v} \text{ or } \frac{\mu_{v1}}{\mu_v} = \sqrt{\frac{v_1}{v}}$$

Likewise, from (I) and (I') there results

$$\frac{\mu_{v1}^2}{\mu_v^2} = \frac{\mu_{\infty} - \mu_{v1}}{\mu_{\infty} - \mu_v} \cdot \frac{v_1}{v}$$

Since $v_1 > v$, $\mu_{v1} > \mu_v$, and therefore $\frac{\mu_{\infty} - \mu_{v1}}{\mu_{\infty} - \mu_v} > 1$, it follows that $\frac{\mu_{v1}^2}{\mu_v^2}$ is always less than $\frac{v_1}{v}$ and approaches this value as a limit. Therefore, as molecular conductivity increases in concentrated solutions, as long as the compound is slightly dissociated, the values of $\frac{\mu_{v1}^2}{\mu_v^2}$ found experimentally will not differ greatly from $\frac{v_1}{v}$ but, with increasing dilution and greater degree of dissociation, $\frac{\mu_{v1}^2}{\mu_v^2}$ will decrease in value and differ more and more from $\frac{v_1}{v}$.

As a result of his conductivity measurements on di- and trichloroacetic and β -resorcylic acids, Wildermann drew the following conclusions:

“(1) For dichloroacetic acid, when $v < 10$ liters the values of $\frac{\mu_{v1}}{\mu_v}$ are less than $\sqrt{\frac{v_1}{v}}$; above 10 liters $\frac{\mu_{v1}}{\mu_v}$ is greater than $\sqrt{\frac{v_1}{v}}$; at dilutions from 800 to 2,000 liters $\frac{\mu_{v1}}{\mu_v}$ becomes almost equal to $\frac{v_1}{v}$. The increase of $\frac{\mu_{v1}}{\mu_v}$ is, therefore, continuous, not only in concentrated solutions, but also in the more dilute, to which the equation $\frac{\mu_{\infty}(\mu_{\infty} - \mu_v)}{\mu_v^2} v = k$ should apply.”

“(2) The same conclusions are even more nearly true in the case of β -resorcylic acid, where the increase of $\frac{\mu_{v1}}{\mu_v}$ is almost proportional to the volume.”

(3) In the case of trichloroacetic acid, with increase in dilution from 20 to 300 liters $\frac{\mu_{v1}}{\mu_v}$ approaches $\sqrt{\frac{v_1}{v}}$; and beyond 300 liters a relation obtains which can be expressed approximately by the dilution law. The fact that the values of $\frac{\mu_{v1}}{\mu_v}$ for solutions more concentrated than 300 liters are not in keeping with the dilution law, was confirmed in a later investigation¹ by Wildermann using an independent method. An explanation of this anomalous condition was offered in a previous paper,² and will not be discussed here.

(4) It had been pointed out by Ostwald, that in aqueous solutions the degree of dissociation of the same dilution of trichloroacetic, dichloroacetic, monochloroacetic, and acetic acids showed a decrease in the order named. A like succession was observed by Wildermann for the same acids in alcohol.

In summing up, Wildermann says that it is possible to apply the Kohlrausch method to the determination of the conductivity of strong organic and inorganic acids in alcoholic solution, but that reliable results could not be obtained for such weak acids as acetic, monochloroacetic, and succinic. However, even in the cases where the method is best applicable, much time and patience on the part of the experimenter are required to obtain results that are at all reliable.

Because of the difficulty which he experienced in applying the Kohlrausch method to the study of the conductivity of weakly dissociated organic acids in absolute alcohol as a solvent, Wildermann employed another method¹ for the investigation of these acids. This consists in the use of a direct current of high voltage (140 to 150 volts). Polarization can be neglected, and since the external resistances are large, the measurement of conductivity resolves itself into the measurement of the strength of the current. This is done comparatively by means of a reflecting galvanometer, the solutions being contained in capillary tubes of varying lengths and diameters. The same conclusions were reached as before, except that the galvanometer method was found susceptible of more general application than that of Kohlrausch.

This method has been found open to objection by Malmström,³ who prefers a method described by Nernst,⁴ whenever small conductivities are to be measured.

In 1902 Hantzsch and Voegelen⁵ found the conductivity method capable of distinguishing between a true acid and a so-called "pseudo acid" which in aqueous solution partly breaks down into the constituent ions of the true acid. The application of the method in this instance depends upon the different behavior of the molecular conductivities of

¹Zeit. phys. Chem., **14**, 247 (1894).

⁴*Ibid.*, **14**, 622 (1894).

²Ber. d. deutsch. chem. Gesell., **26**, 1782 (1893).

⁵Ber. d. deutsch. chem. Gesell., **35**, 1001 (1902).

³Zeit. phys. Chem., **22**, 331 (1897).

true and pseudo acids in aqueous alcoholic solutions containing different percentages of alcohol. If it is desired to test whether a given hydrogen compound is a pseudo acid or not, a true acid with approximately the same affinity constant is selected, and the molecular conductivity of both is determined in aqueous alcohol at a given dilution. Then, without varying the dilution, the percentage of alcohol is increased and the resulting conductivities determined. If the molecular conductivity of the hydrogen compound decreases much more slowly than that of the true acid, it is a pseudo acid. Hantzsch and Voegelen offered no explanation for this difference in behavior, but they supported their discovery with widely different examples.

In the last few years Heinrich Goldschmidt¹ has applied the conductivity method to alcoholic solutions of organic acids, in order to determine the equilibrium hydrogen ion-alcohol-water, and he has succeeded in throwing new light on the mechanism of esterification and on the formation of complex ions.

In his earlier work (1895) on the kinetics of esterification in alcoholic solutions of organic acids, Goldschmidt had observed that the catalytic action of strong acids in accelerating esterification was greatly diminished by the addition of water. He explained this on the assumption that the accelerating action of a strong acid was due to the formation of a complex molecule by union of the acid with alcohol, and that the retardation was brought about by the decomposition of this molecule by water. For example, if hydrochloric acid were acting as the catalyst, a compound $C_2H_5OH \cdot HCl$ would be formed, and this would be acted upon by water according to the equation



For a time² Goldschmidt thought that only the ionized portion of the complex molecule took part in the esterification, and from measurements of reaction velocity he undertook to determine the equilibrium in the reaction



He found that a number of organic acids which were esterified in the presence of hydrochloric acid showed the same retardation when equal volumes of water were added. From this he concluded that his assumption was correct, and for the equilibrium

$$r = \frac{C(C_2H_5OH \cdot H^+) \times C_{H_2O}}{C(H_2O \cdot H^+)}$$

he calculated the equilibrium constant r to be 0.15.

¹Zeit. Elektrochem., **15**, 4 (1909); Zeit. phys. Chem., **70**, 627 (1910); *Ibid.*, **81**, 30 (1912); Zeit. Elektrochem., **20**, 473 (1914); Zeit. phys. Chem., **89**, 129 (1914).

²Zeit. phys. Chem., **60**, 728 (1907).

In 1909 Goldschmidt noticed that when weaker acids, such as trichlorobutyric, picric, etc., were used as accelerators, the effect of water on the reaction velocity could not be calculated by means of the constant $r=0.15$, but that a much smaller value had to be selected. Under these conditions not only the ionized part of the double compound alcohol-acid was acting as catalyzer (according to equation II), but also the undissociated portion (as represented in equation I). Consequently, the constant 0.15 was not wholly dependent upon the relation between the ions, and could not be used to characterize the equilibrium hydrogen ion-alcohol-water. Goldschmidt, therefore, devised a new way of obtaining this equilibrium constant, namely, the determination of the limiting conductivities of acids in absolute and aqueous alcoholic solutions.

The molecular conductivity of an acid in absolute alcohol at infinite dilution is expressed by the well-known equation

$$\mu_0 = u + v \quad (\text{I})$$

where u equals the migration velocity of the cation and v that of the anion. (It is assumed that there are at least two kinds of cations in the solution—free hydrogen ions and the complex ions $(\text{C}_2\text{H}_5\text{OH}, \text{H})^+$; but since the ratio of these two must always be constant they may be considered as one.) As soon as water is added, a new kind of ion is formed— $(\text{H}_2\text{O}, \text{H})^+$. If the concentration of the water added be η mols. per liter, and the migration velocity of the ions $(\text{H}_2\text{O}, \text{H})^+$ be u' , the conductivity at infinite dilution, μ_n , will be expressed by the equation

$$\mu_n = xu + (1-x)u' + v \quad (\text{II})$$

where x represents the fraction of a gram cation which is still present in the original condition (as free or alcoholated hydrogen ion), and $1-x$ the fraction transformed into the hydrated ion $(\text{H}_2\text{O}, \text{H})^+$. Therefore, the equilibrium equation which expresses the distribution of hydrogen ions between alcohol and water, is

$$\frac{x\eta}{1-x} = r$$

whence

$$x = \frac{r}{\eta+r} \text{ and } 1-x = \frac{\eta}{\eta+r}$$

Substituting these values in (II), we have

$$\mu_n = \frac{r}{\eta+r}u + \frac{\eta}{\eta+r}u' + v$$

and, since $v = \mu_0 - u$, this reduces to

$$(\mu_0 - \mu_n)(\eta+r) = (u - u')\eta \quad (\text{III})$$

If we know μ_0 and the values of μ_η corresponding to two or more values of η , the equation can be solved for r , the equilibrium constant, and for $u-u'$, the difference between the migration velocity of the cations in anhydrous alcohol and that of the hydrated ion— $(\text{H}_2\text{O},\text{H})^+$ in aqueous alcohol. Therefore, in order to test the equation, it is only necessary to determine the conductivity at infinite dilution of several organic acids in pure alcohol and in two or more alcohol-water mixtures.

The greatest experimental difficulty in doing this lay in the preparation of pure absolute alcohol. At first¹ metallic calcium was used for this purpose (von Winkler's method), but the alcohol prepared in this way, although practically free from water, was found² to contain considerable amounts of ammonia (formed by the action of water upon the calcium nitride present in the calcium); and hence this method had to be abandoned. After further experimentation a satisfactory product was finally obtained in the following manner:

Ordinary 95 per cent alcohol was allowed to stand in contact with lime for some time and then distilled (Kailan). This treatment reduced the water content to about 0.006-normal, or 0.12 gram per liter. The same process was repeated, this time using a distilling vessel and condenser of copper; and the amount of water present was decreased to 0.003-normal, or 0.06 gram per liter. If a completely anhydrous alcohol was desired, the product of the first distillation was treated with calcium. For this purpose calcium bars were turned on a lathe to remove the coating of hydroxide, and the bright metal was cut into pieces the size of a pea. An amount of calcium equal to ten times the amount of water present (about 0.1 gram) was introduced into the alcohol. The whole was then heated for several hours with a reflux condenser attached, and a rapid stream of dry air was passed through the distillation chamber to remove traces of ammonia. In this way absolute alcohol was obtained having a specific conductivity of 2×10^{-7} .

With a good quality of alcohol in his possession Goldschmidt was ready to test his equation, and he began his study with hydrochloric acid. First, the molecular conductivity in absolute alcohol was measured at dilutions ranging from 10 to 5,120 liters; and from the values obtained for the more dilute solutions μ_0 , the conductivity at infinite dilution was calculated with the aid of Kohlrausch's formula

$$\mu_\infty = \mu_v + a \sqrt[3]{\frac{1}{v}}$$

The mean value of μ_0 proved to be 89. Then the conductivity in aqueous alcohol containing different amounts of water (η) was determined over the same range of dilution, and the limiting conductivity, μ_η , corresponding to each alcohol-water mixture, was estimated as before. The results show that the molecular conductivity of solutions

¹Zeit. Elektrochem., **15**, 4 (1909).

²Zeit. phys. Chem., **81**, 30 (1912).

of hydrochloric acid in alcohol first decreases with increasing percentage of water, then passes through a minimum at $\eta=2$, and finally begins to increase again. μ_{∞} behaves in a similar manner.

Using the value 89 for μ_0 , and combining with it the values of μ_{η} obtained for the different water concentrations (η), Goldschmidt solved equation (III) for r and $u-u'$, and obtained the constants 0.0583 and 42.7 respectively. The high value of $u-u'$ shows that the complex ion $(\text{H}_2\text{O}, \text{H})^+$ travels much more slowly than the free or the alcoholated hydrogen ion. The constancy of r and $u-u'$ is evidence in favor of the correctness of the reasoning by which the equation was developed. In order to determine the limit of applicability of the constants 0.0583 and 42.7, Goldschmidt used these constants to recalculate the values of μ_{η} . He found satisfactory agreement between the calculated values and those obtained experimentally, so long as the percentage of water (η) in the alcohol did not exceed unity. (Beyond this point there was a lack of agreement, caused no doubt by the influence of water upon the migration velocities of the ions.) Thus, Goldschmidt showed that by means of the constants 0.0583 and 42.7 the effect of water on the conductivity of alcoholic solutions of strong acids could be calculated.

TABLE 73.

Acid.	μ_{∞} (Na salt).	μ_{∞} (acid).
Hydrochloric.....	47	89
Sulphosalicylic.....	41	83
Picric.....	51	93
Trichloroacetic.....	46	88
Trinitrobenzoic.....	44	86
Trichlorobutyric.....	45	87
Dichloroacetic.....	48	90
Salicylic.....	44	86

Desiring to adduce further evidence bearing on his theory, Goldschmidt took up a study of the conductivity of sulphosalicylic acid. He found the behavior of this acid to be entirely analogous to that of hydrochloric. The molecular conductivity in alcohol was influenced to the same extent by the addition of water, and the amount of this influence could be calculated with the aid of the constants 0.0583 and 42.7. The limiting conductivity in absolute alcohol (μ_0) was estimated both from the μ_{∞} value of the sodium salt (by the method of Ostwald), and from the μ_{∞} values of the free acid in aqueous alcohol (by means of equation III), and the figure obtained was the same (83) in both cases.

Satisfied with the results of his investigations upon the stronger acids, Goldschmidt next turned his attention to the weaker—picric, trichloroacetic, trinitrobenzoic, trichlorobutyric, dichloroacetic, and salicylic. He observed that in every case the molecular conductivity

increased with increase in the concentration of the water present in the solution. The μ_{∞} values for the weaker acids could not be determined directly, as had been done previously for the strong acids, and Goldschmidt employed the method of Ostwald for calculating the limiting conductivity of an acid from that of its sodium salt. The values obtained are given in table 73, which shows that the difference in the migration velocities of the anions is very slight.

From the μ_{∞} values of the acids, the degrees of dissociation (α) and the affinity constants (k) were calculated. The values of k given in table 74 were obtained for the solutions in absolute alcohol.

TABLE 74.

Acid.	k
Picric.....	1.8×10^{-4}
Trichloracetic.....	1.5×10^{-6}
Trinitrobenzoic.....	8.3×10^{-7}
Trichlorbutyric.....	1.0×10^{-7}
Dichloracetic.....	7.2×10^{-8}
Salicylic.....	2.4×10^{-9}

The influence of water upon the values of k was also investigated, with the result that k was found to increase regularly with increasing concentration of water. The law of this increase was expressed in the form of an equation which Goldschmidt deduced from theoretical considerations.

In conclusion, Goldschmidt showed that the influence of the weaker acids upon the velocity of esterification could be calculated by means of the constant 0.0583. The calculated values agreed very satisfactorily with those obtained experimentally.

This work of Goldschmidt has been discussed at some length, not because it is a final word on the subject with which it deals, but for the reason that it presents an excellent illustration of the ever increasing applicability of the conductivity method to the solution of chemical problems.

EXPERIMENTAL WORK.

REAGENTS.

The alcohol used in this investigation was prepared in the following way: Ordinary 95 per cent alcohol was heated for several days with lime in a copper tank provided with a ground-brass stopper and reflux condenser, and then distilled through a block-tin condenser. The product of this distillation was reheated with fresh lime and again distilled, the first and last portions of the distillate being discarded.

The receiver for the distillate was a 6-liter Jena glass bottle, having a three-holed paraffined cork as stopper. Through one hole passed a siphon, through another an adapter with a glass stopcock, and through the third a calcium chloride-soda lime tube. In this way the alcohol was well protected, during distillation, from impurities in the air, and small quantities sufficient for making up the solutions could be drawn off without exposing the main supply. By exercising extreme care it is possible by this method to obtain alcohol having a specific gravity of 0.78506 to within the limit of error ± 0.00002 . According to Circular 19 of the Bureau of Standards such alcohol is pure. The alcohol employed in the conductivity measurements varied in specific gravity from 0.78506 to 0.78517, the latter containing 99.964 per cent alcohol.

The organic acids were obtained from Kahlbaum and Schuchardt. The same methods of purifying them were employed as when the conductivities of these acids were determined in aqueous solution.¹ After purification they were carefully dried in a vacuum desiccator containing sulphuric acid. Whenever practicable the melting-points of the acids were taken as one criterion of purity.

Aqueous solutions of ammonia were used for titration purposes, since ammonia had been found by Wightman, Wiesel, and Jones² to give the most satisfactory results. These solutions were prepared as follows: Concentrated ammonia was heated and the gas which was given off passed first over sodium hydroxide, which collected a large part of the water-vapor and any carbon dioxide; then over sodium, which absorbed the remainder of the water-vapor; and finally into a weighed quantity of conductivity water in a measuring flask, until the amount necessary to make a 0.1 N solution was dissolved. By diluting this solution with conductivity water any desired strength of ammonia could be obtained. The normality of each solution employed was determined by titration against standard sulphuric acid.

Corallin (rosolic acid) was used as the indicator, because it is sensitive to ammonia and to organic acids, and is not sensitive to carbon dioxide except when the latter is present in fairly large quantity. The end-point with corallin is not quite as sharp and distinct as with phenolphthalein, and considerable practice is necessary before reliable results can be obtained.

APPARATUS.

On account of the high resistance of the alcoholic solutions of the acids, it was found necessary to make use entirely of the cylindrical type of conductivity cell. The method of obtaining the constants of these cells was described by White³ and by Wightman.⁴

¹Amer. Chem. Journ., **44**, 156 (1910); **46**, 56 (1911); **48**, 320, 411 (1912); **50**, 1 (1913).

²Journ. Amer. Chem. Soc., **36**, 2247-2249 (1914).

³Amer. Chem. Journ., **42**, 527 (1909).

⁴*Ibid.*, **42**, 527 (1909); **44**, 64 (1911).

Since the percentage temperature coefficients of conductivity for substances dissolved in alcohol, as well as the coefficient of expansion of the alcohol itself, are so large, it is necessary to regulate the temperature as closely as possible. This was done by the combination of a specially devised gas-regulator and thermo-regulator. These have already been described in a paper by Davis and Hughes.¹

The constant-temperature baths were of the improved form designed by Davis,² of this laboratory. These baths are of about 60 liters capacity and are made of copper. Heat is applied to a heavy iron pipe outside the bath, and water is kept circulating through this pipe by means of propellers. Only a small portion of the water in the thermostat comes into immediate contact with the heated surface, and this portion is subsequently mixed with the main body of water, thereby securing much more even distribution of temperature. In these baths ordinarily the temperature does not vary more than 0.02°, which is sufficiently constant for our purpose. With greater precautions as to insulation against changes in temperature, and with further modification of the thermo-regulator, the variation can be decreased to a few thousandths of a degree.

A $\frac{1}{12}$ -horsepower direct-current motor served as the source of power for the stirrers, the power being transmitted by belt drives. The motor proved to be a great improvement over the hot-air engines formerly used.

The thermometers were of the differential Beckman type, and were carefully compared with a standard Reichsanstalt thermometer, which had been calibrated also at the United States Bureau of Standards.

The resistance-box which was used throughout this entire investigation had also been calibrated at the Bureau of Standards. A very fine Kohlrausch slide-wire bridge was employed, by means of which it was possible to read distances on the slide-wire corresponding to tenths of a millimeter (the total length of the wire was 5 meters).

Flasks, pipettes, and burettes for measuring purposes were in all cases carefully calibrated.

PROCEDURE.

The solutions of the organic acids in alcohol were made up in 200 c.c. Jena measuring flasks calibrated for 25°. The quantity of dried and purified acid necessary to make a solution of the required normality was weighed out on a watch-glass, and was washed off through a funnel into one of the measuring flasks. The flask was shaken until all the acid had dissolved; it was then filled to the neck with alcohol and suspended in the 25° bath. When temperature equilibrium was reached it was filled to the mark. In the meantime a conductivity cell was thoroughly washed with pure alcohol and dried with filtered dry air.

¹*Zeit. phys. Chem.*, **85**, 519 (1913).

²*Carnegie Inst. Wash. Pub. No.* **210**, 121 (1915).

It was then nearly filled with the solution which had been made up and placed in the 15° bath. The measuring-flask containing the remainder of the solution was returned to the 25° bath. In this way four dilutions of each acid were prepared—N/8, N/32, N/128 and N/512; and the four cells containing them placed in the 15° bath. In addition, a fifth cell was employed to measure the conductivity of the pure solvent.

After the cells had remained in the 15° bath for at least an hour, the conductivities of the solutions were measured. Titrations of the acids against the standard ammonia were made simultaneously with the conductivity measurements. For this purpose 10 c.c. of the solution in question were taken, by means of a pipette, from the proper measuring flask in the 25° bath. A second titration in each case served to confirm the results of the first.

When the conductivities of the four solutions and of the alcohol had been determined at 15°, the cells were removed to the 25° bath; and after the lapse of an hour measurements were made as before. The same procedure was followed for the determinations at 35°.

At first thought it would seem probable that keeping the solutions in the flasks at a constant temperature (25°), and subjecting the solutions in the cells to changes in temperature (15° to 35°) would produce a change in the rates of esterification. If this were true, the normalities of the solutions in the cells would be different from the values obtained by the titration of the solutions in the flasks, and a considerable error would be introduced. It was found, however, that there was no appreciable difference in the amount of acid present at any moment in a given solution, whether the solution was kept in the 25° bath continuously for 8 hours, or whether it was transferred from one bath to another during this time. The reason for this is no doubt to be found in the extremely slow rate at which, under the conditions of this investigation, esterification takes place.

Although it is reasonably certain that variation in the temperature has no measurable effect upon the rate of esterification in alcoholic solutions of the organic acids, this variation does alter to a considerable extent, the volume, and therefore the concentration, of these solutions. For example, a solution which has a volume of 1,000 c.c. at 25°, contracts to 989.23 c.c. when cooled to 15°, and expands to 1,011.14 c.c. when warmed to 35°. Because of this fact a correction had to be applied to the volume calculated from titration, before molecular conductivity can be estimated at 15° and 35°. This correction was made in the following way: Let us suppose that the normality of a given solution at 25°, as determined by titration against ammonia, is N_{25} . The normality at 15°, N_{15} , would then be expressed by the ratio $\frac{N_{25}}{0.98923}$; and the true volume at 15° (*i. e.*, the number of liters which contain a gram molecular weight of the dissolved acid) would be the

reciprocal of this ratio, or $\frac{0.98923}{N_{25}}$. Similarly, the normality at 35° would be $\frac{N_{25}}{1.01114}$ and the volume would be $\frac{1.01114}{N_{25}}$.

RESULTS.

In the table of conductivity results (table 75), V_m is the volume at which the solutions were made up; V_c is the corrected volume. The corrections were applied in the manner just described, both for expansion or contraction of the alcohol and for change in the concentration of the acid due to the formation of ester. Molecular conductivity, μ_v , was calculated in the usual manner.

A word of explanation should be added in regard to the method of calculating temperature coefficients of conductivity. The formulæ generally employed in the determination of these coefficients are $T = \frac{\mu_{t'} - \mu_t}{t' - t}$ and $\Delta = \frac{T}{\mu_t}$ where μ_t and $\mu_{t'}$ represent the molecular conductivities of the same solution at t and t' , respectively ($t' > t$); T is the temperature coefficient expressed in conductivity units, and Δ is the percentage temperature coefficient. But these formulæ as such are not applicable to alcoholic solutions of organic acids, because the true volume (V_c) of a given solution is different at different temperatures (due to the causes already described). For example, in the case of benzoic acid (see table 75), the N/8 solution was found to have a volume of 7.945 at 15°, of 8.05 at 25°, and of 8.15 at 35°. Before the conductivities of these three solutions can be compared they must be reduced to values corresponding to the same volume. For the sake of simplicity V_c at 25° is taken as the standard of reference. The reduction of μ_v at 15° to V_c at 25° is made in the following way: The specific conductivity at 15° ($\frac{0.002892}{7.945} = 0.000364$) is multiplied by the difference in volume at 15° and 25° ($8.05 - 7.945 = 0.105$). The product (0.000038) is added to the molecular conductivity at 15° (0.002892), giving 0.002930, which represents the molecular conductivity at 15° of a solution of volume 8.05. This value (0.002930) and the value of μ_v at 25° (0.004073) can then be substituted for μ_t and $\mu_{t'}$ in the above equations, and T and Δ are found to be 0.0001143 and 3.90 respectively. Similarly, the specific conductivity at 35° ($\frac{0.005444}{8.15} = 0.000668$) is multiplied by the difference in volume at 25° and 35° ($8.15 - 8.05 = 0.10$). The product (0.000067) is subtracted from the molecular conductivity at 35° (0.005444), giving 0.005377, which represents the molecular conductivity at 35° of a solution of volume 8.05. This value (0.005377) and the value of μ_v at 25° (0.004073) can then be substituted for $\mu_{t'}$ and μ_t in the formulæ, and T and Δ are determined to be 0.0001304 and 3.20 respectively.

TABLE 75.—Conductivity results.

Acid.	Molecular conductivity.						Temperature coefficients of conductivity.		Specific conductivity of alcohol.	
	V_m	V_c	μ_0 15°	V_c	μ_0 25°	V_c	μ_0 35°	15 to 25°		25 to 35°
Phenylacetic.....	8	7.94	0.004176	8.04	0.005660	8.13	0.007325	<i>cond. units, p. cl.</i>	<i>cond. units, p. cl.</i>	At 15°, 0.000168
	32	32.70	0.01122	33.42	0.01614	34.08	0.02167	0.001431	0.001584	At 25°, 0.000149
	128	146.9	0.04392	152.2	0.06347	156.9	0.08598	0.00467	0.00510	At 35°, 0.000125
	512	537.9	0.1581	545.0	0.2245	552.2	0.2976	0.01797	0.01993	
Oxyisobutyric.....	8	7.99	0.005234	8.08	0.006666	8.17	0.008346	0.0643	0.0692	3.08
	32	32.71	0.01429	33.33	0.01813	33.84	0.02264	0.001374	0.001584	2.38
	128	139.5	0.05022	143.3	0.06391	147.3	0.07969	0.00357	0.00417	2.30
	512	537.6	0.1699	543.8	0.2208	550.1	0.2718	0.01232	0.01383	2.16
Brompalmitic.....	8	7.97	0.007014	8.06	0.009027	8.16	0.01142	0.0489	0.0479	2.17
	32	33.07	0.01776	33.52	0.02316	33.99	0.02964	0.001934	0.00225	2.49
	128	151.8	0.07013	154.9	0.09248	158.1	0.1183	0.00516	0.00607	2.62
	512	540.0	0.2349	546.1	0.3129	552.5	0.3950	0.02092	0.0234	2.53
Malonic.....	8	8.12	0.0190	8.13	0.0237	8.18	0.0319	0.0753	0.0781	2.50
	32	32.9	0.0434	33.2	0.0555	33.7	0.0737	0.0046	0.0079	3.39
	128	129.3	0.0775	129.5	0.0985	129.6	0.1351	0.0113	0.0192	3.59
	512	512.8	0.2533	514.9	0.3160	518.1	0.4338	0.0207	0.0359	3.69
Ethylmalonic.....	8	7.96	0.01937	8.05	0.02590	8.15	0.03346	0.0613	0.1145	3.64
	32	32.28	0.06333	32.70	0.08345	33.13	0.1066	0.00631	0.00715	2.76
	128	134.9	0.2459	137.1	0.3236	140.6	0.4134	0.01930	0.02175	2.60
	512	532.4	0.9924	538.5	1.295	545.1	1.624	0.0727	0.0795	2.46
Diethylmalonic.....	8	7.95	0.02857	8.05	0.03860	8.14	0.05022	0.291	0.309	2.39
	32	32.25	0.06042	32.66	0.08044	33.04	0.1034	0.00967	0.01107	2.87
	128	136.0	0.1257	139.1	0.1732	142.2	0.2279	0.01845	0.02376	2.95
	512	533.3	0.2527	539.4	0.3441	546.0	0.4494	0.0446	0.0497	2.87
Propylmalonic.....	8	7.95	0.03271	8.04	0.04220	8.13	0.05280	0.0885	0.0999	2.90
	32	32.21	0.07995	32.63	0.1049	33.09	0.1326	0.00912	0.01002	2.37
	128	136.0	0.2739	139.1	0.3663	141.4	0.4628	0.0239	0.0259	2.47
	512	533.3	1.021	539.4	1.346	545.7	1.692	0.0862	0.0890	2.43
								0.313	0.326	2.42

Dipropylmalonic.....	8	8.12	0.03354	8.22	0.04453	8.33	0.05772	0.001619	2.39	0.00187	2.23	At 15°, 0.000067
	32	31.29	0.06759	31.84	0.09058	32.45	0.1178	0.00340	2.62	0.00380	2.32	At 25°, 0.000071
	128	130.3	0.1416	131.9	0.1889	133.6	0.2442	0.00823	2.59	0.00994	2.48	At 35°, 0.000074
	512	540.3	0.3031	548.8	0.4078	558.3		0.0299	2.70	0.0351	2.50	
Butylmalonic.....	8	7.97	0.0169	8.08	0.0219	8.19	0.0277	0.0048	2.82	0.0054	2.47	At 15°, 0.000078
	32	32.89	0.0269	33.65	0.0363	34.26	0.0479	0.0088	3.20	0.0108	2.97	At 25°, 0.000075
	128	142.3	0.0549	147.8	0.0794	153.2	0.1069	0.0224	3.93	0.0237	2.98	At 35°, 0.000071
	512	535.0	0.1257	547.6	0.1780	555.0	0.2364	0.0493	3.83	0.0553	3.10	
Allylmalonic.....	8	7.97	0.01309	8.06	0.01757	8.15	0.02304	0.00433	3.27	0.00522	2.97	At 15°, 0.000149
	32	33.07	0.02867	33.52	0.03882	34.01	0.05068	0.00976	3.36	0.01108	2.85	At 25°, 0.000137
	128	142.4	0.08701	145.2	0.1170	148.6	0.1491	0.0283	3.19	0.0286	2.44	At 35°, 0.000125
	512	540.6	0.2822	546.7	0.3756	553.4	0.4798	0.0902	3.16	0.0984	2.62	
Benzylmalonic.....	8	7.95	0.03391	8.04	0.04200	8.13	0.05155	0.00771	2.25	0.00898	2.14	At 15°, 0.000149
	32	32.23	0.04880	32.64	0.06189	33.04	0.07738	0.01167	2.36	0.01455	2.35	At 25°, 0.000137
	128	134.7	0.1043	137.1	0.1361	139.4	0.1723	0.0299	2.81	0.0334	2.45	At 35°, 0.000125
	512	533.0	0.3017	539.1	0.4032	545.7	0.5091	0.0980	3.21	0.0997	2.47	
Monobromsuccinic.....	8											At 15°, 0.000173
	32	33.02	0.0426	33.65	0.0556	34.26	0.0736	0.0122	2.81	0.0167	3.00	At 25°, 0.000152
	128	150.1	0.0827	157.1	0.1177	162.5	0.1589	0.0308	3.54	0.0359	3.05	At 35°, 0.000129
	512	539.1	0.2167	546.4	0.3087	553.4	0.4112	0.0891	4.06	0.0973	3.15	
Dibromsuccinic.....	8	7.96	0.01839	8.06	0.02441	8.16	0.03213	0.00579	3.11	0.00733	3.00	At 15°, 0.000133
	32	32.31	0.03648	32.76	0.04816	33.15	0.06206	0.01117	3.02	0.01317	2.74	At 25°, 0.000140
	128	136.4	0.09984	139.1	0.1289	142.2	0.1654	0.0281	2.79	0.0329	2.55	At 35°, 0.000145
	512	533.3	0.3130	539.4	0.4051	546.0	0.5105	0.0885	2.80	0.0992	2.45	
Sebacic.....	8	8.71	0.001794	8.83	0.002411	8.95	0.003141	0.000592	3.25	0.000688	2.85	At 15°, 0.000205
	32	34.20	0.004001	34.79	0.005566	35.44	0.007549	0.001496	3.68	0.001845	3.32	At 25°, 0.000241
	128	138.7	0.01387	140.6	0.01884	142.6	0.02510	0.00478	3.40	0.00591	3.14	At 35°, 0.000271
	512	579.5	0.04694	593.1	0.06465	605.1	0.08592	0.01661	3.46	0.01957	3.03	
Thiodiglycolic.....	8	8.65	0.02326	8.76	0.02951	8.88	0.03746	0.00596	2.53	0.00745	2.52	At 15°, 0.000205
	32	33.95	0.03263	34.57	0.04269	35.15	0.05557	0.00947	2.85	0.01196	2.80	At 25°, 0.000241
	128	138.1	0.05261	140.0	0.07042	141.7	0.09281	0.01708	3.20	0.02128	3.02	At 35°, 0.000271
	512	568.2	0.1119	579.7	0.1501	587.5	0.2015	0.0359	3.14	0.0487	3.24	
Benzilic.....	8	7.96	0.01660	8.05	0.02200	8.14	0.02799	0.00521	3.10	0.00568	2.58	At 15°, 0.000441
	32	32.17	0.05527	32.56	0.07267	33.04	0.09271	0.01673	2.99	0.01869	2.57	At 25°, 0.000379
	128	134.0	0.2176	137.1	0.2882	141.0	0.3711	0.0656	2.95	0.0726	2.52	At 35°, 0.000320
	512	531.8	0.8849	537.9		544.8	1.217	0.260	2.90			

Table 76. Conductivity results. (Contd.)

Acid	Molar conductivity					Temperature dependence of conductivity			Approximate viscosity of solvent
	V_m	V_2	μ_0 15°	V_2	μ_0 25°	V_2	15° 25°	25° 35°	
Malonic	2	7.95	6.1564	2.94	6.1322	2.34	6.2444	6.2444	2.24
	22	32.24	6.2812	22.26	6.2762	22.22	6.2762	6.2762	2.22
	126	126.2	6.1977	126.2	6.1977	126.1	6.1977	6.1977	2.27
Fumaric	2	7.92	6.0671	2.94	6.0671	2.34	6.0671	6.0671	2.24
	22	32.24	6.0671	22.26	6.0671	22.22	6.0671	6.0671	2.22
	126	126.2	6.0671	126.2	6.0671	126.1	6.0671	6.0671	2.27
Maleic	2	7.95	6.0671	2.94	6.0671	2.34	6.0671	6.0671	2.24
	22	32.24	6.0671	22.26	6.0671	22.22	6.0671	6.0671	2.22
	126	126.2	6.0671	126.2	6.0671	126.1	6.0671	6.0671	2.27
Mesaconic	2	7.95	6.0671	2.94	6.0671	2.34	6.0671	6.0671	2.24
	22	32.24	6.0671	22.26	6.0671	22.22	6.0671	6.0671	2.22
	126	126.2	6.0671	126.2	6.0671	126.1	6.0671	6.0671	2.27
Phenylpropionic	2	7.95	6.0671	2.94	6.0671	2.34	6.0671	6.0671	2.24
	22	32.24	6.0671	22.26	6.0671	22.22	6.0671	6.0671	2.22
	126	126.2	6.0671	126.2	6.0671	126.1	6.0671	6.0671	2.27
Acetic	2	7.95	6.0671	2.94	6.0671	2.34	6.0671	6.0671	2.24
	22	32.24	6.0671	22.26	6.0671	22.22	6.0671	6.0671	2.22
	126	126.2	6.0671	126.2	6.0671	126.1	6.0671	6.0671	2.27
Benzoic	2	7.95	6.0671	2.94	6.0671	2.34	6.0671	6.0671	2.24
	22	32.24	6.0671	22.26	6.0671	22.22	6.0671	6.0671	2.22
	126	126.2	6.0671	126.2	6.0671	126.1	6.0671	6.0671	2.27

<i>m</i> -Chlorbenzoic.....	8	7.94	0.01136	8.04	0.005422	8.15	0.007153		0.001641	3.03	At 15°, 0.000159
	32	32.84	0.04907	33.40	0.01610	33.79	0.02149	0.00455	3.94	0.00514	At 25°, 0.000139
	128	147.8	0.1829	151.7	0.06978	157.4	0.09523	0.01942	3.86	0.02200	At 35°, 0.000117
<i>m</i> -Nitrobenzoic.....	512	537.9	0.2556	545.0	0.2556	552.2	0.3402	0.0707	3.81	0.0802	3.14
	8	7.98	0.005725	8.08	0.007470	8.17	0.009575	0.001680	2.90	0.001995	At 15°, 0.000133
	32	32.65	0.01786	33.07	0.02308	33.54	0.02915	0.00522	2.89	0.00566	At 25°, 0.000139
Dinitrobenzoic.....	128	140.8	0.07293	143.5	0.09414	146.9	0.1178	0.01981	2.66	0.0210	At 35°, 0.000145
	512	537.9	0.2754	544.1	0.3526	550.7	0.4362	0.0740	2.66	0.0784	2.23
	8	7.95	0.01947	8.04	0.02554	8.13	0.03290	0.00584	2.96	0.00700	At 15°, 0.000090
Picric.....	32	32.28	0.03083	32.72	0.04113	33.15	0.05377	0.00988	3.16	0.01194	At 25°, 0.000103
	128	135.6	0.4427	138.7		141.4					At 35°, 0.000113
	512	532.7	0.4427	538.8	0.4980	545.1	0.6192	0.0502	1.12	0.1140	2.29
Sulphosalicylic.....	8	8.69	2.934	8.80	3.502	8.91	4.120	0.531	1.79	0.567	At 15°, 0.000205
	32	34.02	5.202	34.64	6.264	35.15	7.392	0.967	1.82	1.021	At 25°, 0.000241
	128	138.3	9.569	140.3	11.445	142.2	13.484	1.738	1.79	1.859	At 35°, 0.000271
<i>o</i> -Aminobenzoic.....	512	570.8	18.192	585.8	22.031	597.3	26.106	3.361	1.80	3.572	1.62
	8	7.97	16.63	8.06		8.15	25.63				At 15°, 0.000066
	32	32.24	26.60	32.68	30.68	33.14	34.87	3.72	1.38	3.71	At 25°, 0.000077
<i>p</i> -Aminobenzoic.....	128	137.6	36.46	140.7	42.81	143.9	50.06	5.53	1.48	6.13	At 35°, 0.000088
	512	533.0	40.18	539.4	44.35	546.0	55.94	7.18	1.76	7.42	1.55
	8	7.98	0.03531	8.07	0.04290	8.17	0.05160	0.00718	2.01	0.00808	At 15°, 0.000090
<i>o</i> -Toluic.....	32	32.62	0.02760	33.07	0.03400	33.53	0.04242	0.00602	2.15	0.00784	At 25°, 0.000102
	128	139.9	0.05148	142.7	0.06279	145.5	0.07697	0.01028	1.96	0.01270	At 35°, 0.000113
	512	534.4	0.1817	540.5	0.2092	546.9		0.0254	1.38		
<i>p</i> -Aminobenzoic.....	8	7.95	0.2020	8.05	0.2427	8.14	0.2897	0.0383	1.87	0.0425	At 15°, 0.000090
	32	32.36	0.2397	32.80	0.2910	33.23	0.3512	0.0480	1.98	0.0537	At 25°, 0.000102
	128	138.1	0.2665	141.4	0.3331	143.8	0.4128	0.0602	2.21	0.0728	At 35°, 0.000113
<i>o</i> -Toluic.....	512	533.3	0.2165	539.7	0.2672	545.7	0.3231	0.0481	2.20	0.0524	1.96
	8	7.98	0.005429	8.08	0.006721	8.17	0.008174	0.001238	2.24	0.001357	At 15°, 0.000090
	32	32.63	0.01299	33.07	0.01637	33.48	0.01992	0.00320	2.43	0.00331	At 25°, 0.000102
<i>o</i> -Toluic.....	128	140.0	0.04298	142.7	0.05680	144.7	0.06917	0.01299	2.96	0.01141	At 35°, 0.000113
	512	537.3	0.1230	543.5	0.1745	549.8	0.2078	0.0501	4.03	0.0309	1.77

DISCUSSION OF THE RESULTS.

The most striking feature of the conductivities of the organic acids in alcohol, as shown by an examination of table 75, is their extremely small value. Wakeman,¹ in the course of his work on alcohol-water mixtures, plotted curves of conductivity of the organic acids against percentage alcohol, and, on extending the curves in the direction of 100 per cent alcohol, found that they apparently approached zero conductivity as a limit. As can be seen from our results, the conductivities do not actually approach zero, but they never exceed 2, and in the great majority of cases fall below unity. On account of the extremely high resistances offered by alcoholic solutions of the organic acids, Wildermann abandoned the Kohlrausch method as a means of studying the conductivity of these solutions. The difficulty which he experienced was obviated by the authors, by the use of cells with much smaller constants than those he employed. Even with this improvement, it was found necessary to discard all of the very weak organic acids, such as the members of the acetic-acid series.

The conductivities of the organic acids in alcohol are several hundred times smaller than the conductivities of the same acids in water. When we consider the fact that alcohol has from one-fourth to one-fifth the dissociating power of water, as shown by the dissociation of strong electrolytes in these solvents, the above fact does not at present seem to admit of any very satisfactory explanation.

The percentage temperature coefficients of conductivity vary from 2.5 to 4 per cent, and decrease with rise in temperature. They are uniformly higher than the corresponding values in aqueous solutions, which range from 1 to 2.5 per cent. In the light of the work that has been done in this laboratory, these results suggest the following possibilities:

(1) It might be that there is greater alcoholation in alcoholic solution than hydration in aqueous solution, and that the amount of alcoholation decreases with rise in temperature. This view, however, is not substantiated by previous experiences. The alcoholates may be more unstable with rise in temperature than the hydrates, but alcohol seems in general to have far less power to combine with dissolved substances than water.

(2) If the temperature coefficient of fluidity of alcohol were greater than that of water, the ions in alcoholic solutions would have greater freedom of movement than in aqueous solutions. This would account for the larger temperature coefficients of conductivity in alcoholic solutions. Unfortunately, such is not the case. The temperature coefficient of fluidity of water is greater than that of alcohol, as can

¹*Zeit. phys. Chem.*, **11**, 49 (1893); *Ibid.*, **14**, 247 (1894).

be seen from the following values calculated from the results of Wightman, Davis, Holmes, and Jones:¹

TABLE 76.—*Fluidities and temperature coefficients of fluidity.*

	Fluidities.			Temperature coefficients of fluidity.	
	15°	25°	35°	15 to 25°	25 to 35°
Water.....	88.18	112.23	138.89	2.73	2.37
Alcohol....	77.45	94.88	114.80	2.25	2.10

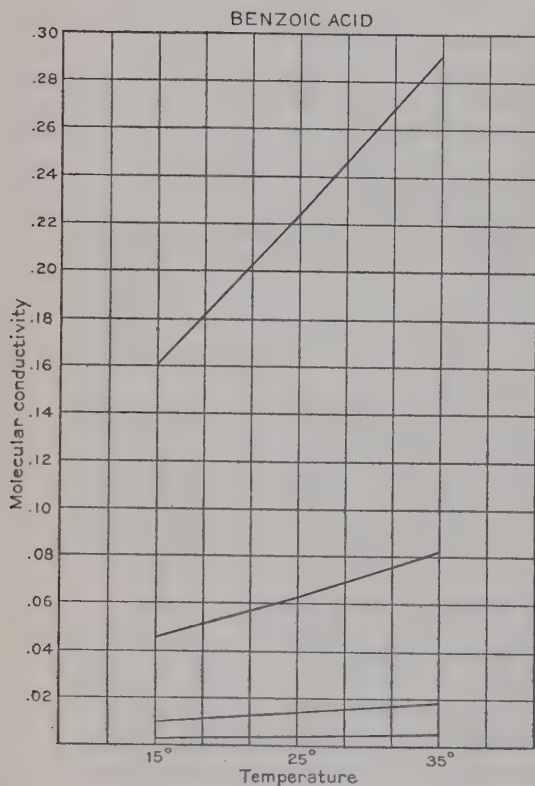


FIG. 13.

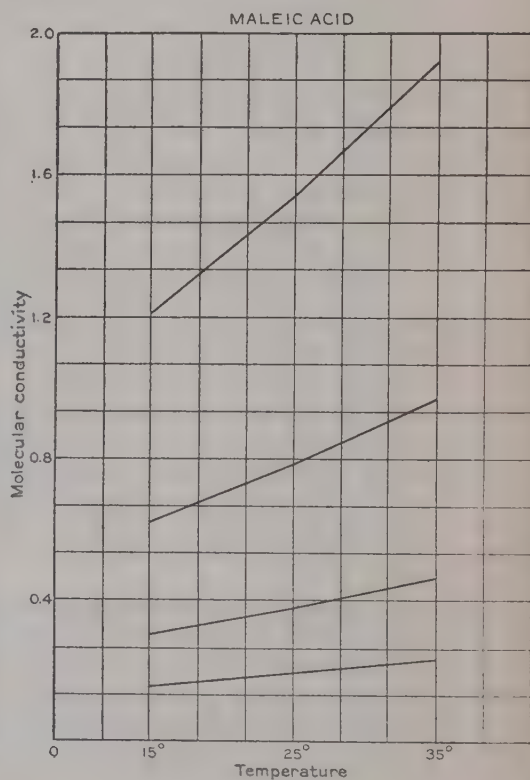


FIG. 14.

Nevertheless, it is possible that the greater expansion of alcohol with rise in temperature affords the ions greater freedom of movement.

(3) A suggestion which seems to be far more probable than either of the preceding, is that the association of alcohol is affected to a less extent by rise in temperature than is the association of water. If this be true, the dissociating power of alcohol relative to that of water will

¹Journ. Chim. Phys., **12**, 406 (1914).

become greater with rise in temperature. This would explain the greater temperature coefficients of conductivity of alcoholic solutions.

The increase in conductivity with rise in temperature can be seen from figures 13 and 14. The curves have very much the appearance of those for aqueous solutions. This suggests the thought that perhaps the increase in molecular conductivity in alcohol with rise in temperature is, as in aqueous solutions, a parabolic function, and that the Euler equation,

$$\mu_v = \mu_0 + at - bt^2$$

applies to both. This will be tested in later work by determining the conductivities of some of the acids at temperatures other than 15°, 25°, and 35°, and comparing the results obtained with those calculated from the above equation.

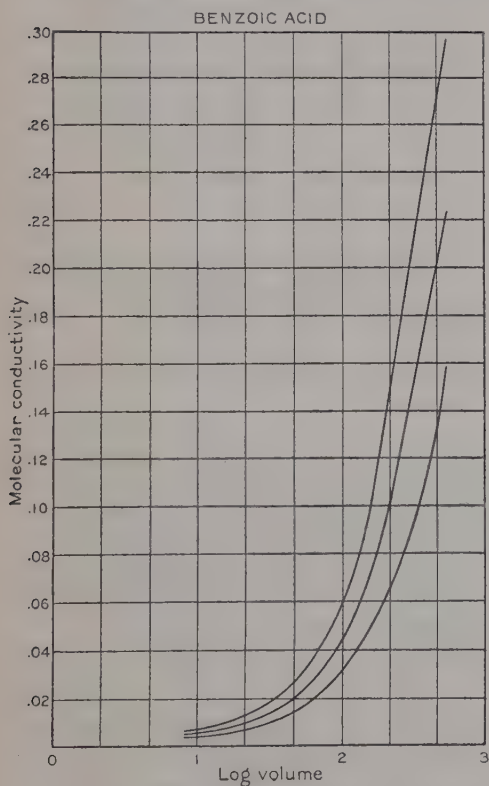


FIG. 15.

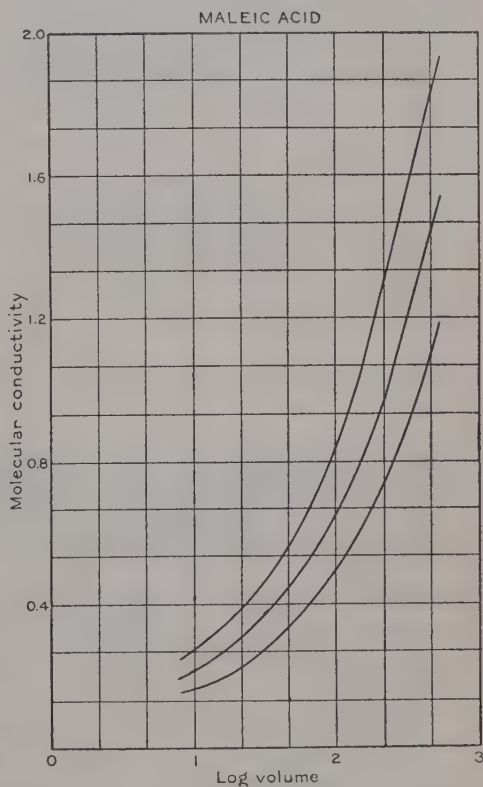


FIG. 16.

The effect of increase in dilution is to increase the molecular conductivity. The increase in conductivity in many cases is almost proportional to the volume. This relation is shown graphically in figures 15 and 16.

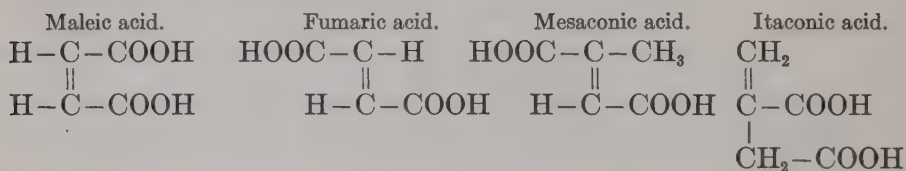
A knowledge of the extent to which organic acids are dissociated in alcoholic solution would be highly desirable. It is hoped that a method

for the determination of percentage dissociation will be worked out here in the near future. Goldschmidt¹ obtained values for the limiting conductivities of several organic acids in alcohol from the μ_{∞} values of their sodium salts. These varied from 83 to 93, depending on the nature of the acid. It has not yet been found practicable to determine the limiting conductivities of the organic acids studied in this investigation, but as a result of Goldschmidt's work it is certain that they do not differ greatly from 90. If this be the case, the dissociation of the organic acids investigated by the authors, as determined by conductivity, do not in any case exceed 2 per cent, even in N/512 solutions.

RELATION BETWEEN COMPOSITION AND CONDUCTIVITY.

In his classical study of the conductivity of aqueous solutions of organic acids, to which reference has already been made, Ostwald² pointed out a number of relations between composition and molecular conductivity. The validity of these relations has been confirmed by the work which has been in progress in this laboratory for the past fifteen years. In view of this, an examination of the results obtained for alcoholic solutions, in the attempt to discover similar relations, should prove to be interesting.

Take the following compounds:



The conductivity of maleic acid (table 75) is many times that of fumaric. This fact is in keeping with the results obtained in aqueous solution,³ and with the present conception of the configuration of these acids. Mesaconic acid is a methyl substitution product of fumaric acid, and its conductivity is of the same order of magnitude as that of fumaric acid. Itaconic acid, which is isomeric with mesaconic acid, but which has very different constitution, shows much higher conductivity.

Malonic acid, at a volume at 32 and at 25°, has a molecular conductivity of 0.055. Under the same conditions, ethylmalonic acid has a conductivity of 0.083; diethylmalonic 0.080; propylmalonic 0.105; dipropylmalonic 0.090; butylmalonic 0.036; allylmalonic 0.039; and benzylmalonic 0.062.

The above results show that the introduction of an ethyl group increases the conductivity, while the introduction of a second ethyl group

¹Zeit. Elektrochem., **15**, 4 (1909); Zeit. phys. Chem., **30**, 627 (1910); **81**, 30 (1912). Zeit. Elektrochem., **20**, 473 (1914); Zeit. phys. Chem., **89**, 129 (1914).

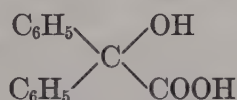
²Zeit. phys. Chem., **3**, 170, 241, 369 (1889).

³Carnegie Inst. Wash. Pub. No. **170**, 113 (1912).

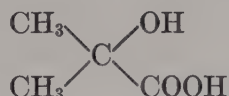
tends to decrease the conductivity of the ethylmalonic acid. Propylmalonic acid has uniformly higher conductivity than ethylmalonic, and the conductivity of the dipropyl acid is uniformly higher than that of the diethyl. Just as diethylmalonic acid has smaller conductivity than ethylmalonic, so dipropylmalonic acid has smaller conductivity than propylmalonic.

Butylmalonic and allylmalonic acids, at the dilution in question, have smaller conductivities than malonic acid itself; but as the dilution increases, the conductivity of allylmalonic acid becomes greater than that of malonic acid.

Benzylmalonic acid has greater conductivity than malonic, but less than ethylmalonic acid. This is especially interesting, in consideration of the fact that, in general, a phenyl derivative of an acid has much greater conductivity than the corresponding methyl derivative; *e. g.*, the conductivity of acetic acid in alcohol is so small that it can not be accurately measured. On the other hand, benzoic acid has a conductivity of 0.014. Again, benzilic acid having the formula



has a much greater conductivity than the corresponding methyl derivative, oxyisobutyric acid



This is in keeping with the results obtained for these acids in aqueous solution,¹ and with the general observation that the replacement of a methyl group by a phenyl group increases the conductivity.

Phenylpropionic acid, $\text{C}_6\text{H}_5 - \text{C} = \text{C} - \text{COOH}$, has a conductivity many times larger than that of cinnamic acid



This is in accord with what was found for these same acids in aqueous solutions.

Take the following series:

Benzoic acid..... $\text{C}_6\text{H}_5\text{COOH}$	1.3.5 dinitrobenzoic acid... $\text{C}_6\text{H}_3(\text{NO}_2)_3\text{COOH}$
<i>m</i> -chlorbenzoic acid.... $\text{C}_6\text{H}_4\text{ClCOOH}$	<i>o</i> -toluic acid..... $\text{C}_6\text{H}_4\text{CH}_3\text{COOH}$
<i>m</i> -nitrobenzoic acid.... $\text{C}_6\text{H}_4\text{NO}_2\text{COOH}$	<i>p</i> -toluic acid..... $\text{C}_6\text{H}_4\text{CH}_3\text{COOH}$

The conductivities of benzoic acid and of orthotoluic acid are about equal, whereas the conductivity of *p*-toluic acid is very much less. That the same relation holds also for other substituent groups may

¹Carnegie Inst. Wash. Pub. **170**, 115, 132 (1912).

be seen from the results obtained a year ago by Wightman, Wiesel, and Jones.¹ For example, the conductivities of *o*-chlorbenzoic acid and of *o*-nitrobenzoic acid are approximately the same as that of benzoic, but the conductivities of the corresponding para-acids are considerably less.

It is well established that in aqueous solution the conductivity of benzoic acid is somewhat increased by the introduction of methyl, chlorine, or the nitro group, in the para position, and enormously increased by the introduction of one of these groups in the ortho position. In contradistinction to this, the effect of these groups upon the conductivity in alcoholic solution appears to be negative. Just the opposite is true if the chlorine or nitro group occupies the meta position, as can be seen from the data. In these cases the conductivity of benzoic acid is somewhat increased.

The introduction of a second nitro group into *m*-nitrobenzoic acid still further increases the conductivity. While benzoic acid, C_6H_5COOH ,

has a conductivity of only 0.015, phthalic acid, $C_6H_4 \begin{matrix} \nearrow COOH \\ \searrow COOH \end{matrix}$ ^a a dicarboxy derivative, has a conductivity of 0.108, which is seven times as great. This same relation holds in aqueous solutions.²

Of all the acids studied in this investigation with one exception, picric acid, $C_6H_2(NO_2)_3OH$, is the strongest. The only stronger acid in alcoholic solutions is sulphosalicylic, which has a conductivity approaching that of hydrochloric acid in this solvent. This is in general analogous to what was found when these compounds were dissolved in water,³ sulphosalicylic acid in water having almost exactly the same conductivity as hydrochloric acid in that solvent.

In order to compare the conductivities of the above-named organic acids in alcohol with the conductivities of these same compounds in water, reference must be had to publication of the Carnegie Institution of Washington No. 170.

¹Journ. Amer. Chem. Soc., **36**, 2251-2252 (1914).

²*Ibid.*, 120, 121.

³Carnegie Inst. Wash. Pub. No. **170**, 116, 133 (1912).

CHAPTER VIII.

CONDUCTIVITIES, TEMPERATURE COEFFICIENTS OF CONDUCTIVITY, AND PERCENTAGE DISSOCIATION OF SOME RATHER UNUSUAL SALTS IN AQUEOUS SOLUTION.

BY CHARLES WATKINS.

This investigation is a contribution to the study of the conductivity, temperature coefficients of conductivity, and dissociation of electrolytes in aqueous solutions. It is a continuation of the work begun by Jones and West¹ in 1905, and which has been in progress continuously since that time. After studying thirty-two substances, organic and inorganic, with special reference to the effects of temperature over a range of 0° to 35°, Jones and West reached the following conclusions:

1. A large increase in conductivity due to greater ionic mobility accompanies a rise in temperature.

2. A rise in temperature brings about a slight decrease in dissociation. This is in accord with the law of Dutoit and Aston, connecting the association of a solvent with its dissociating power, and is in harmony with the results of Ramsey and Shields, showing the relation between the dissociating action of water and rise in temperature.

3. Temperature coefficients of conductivity expressed in percentage units decrease with rise in temperature.

4. The temperature coefficients of conductivity expressed in conductivity units, in the case of salts, increase with rise in temperature, while in the case of acids they decrease.

Jones and Jacobson² next investigated 35 compounds over the same range of temperature used by West, and found that:

1. The molecular conductivity of electrolytes in aqueous solutions increase as a parabolic function of the temperature from 0° to 35°.

2. Hydrolysis is a source of error in obtaining the value of μ_{∞} .

3. The conductivity of water is a linear function of the temperature.

4. Salts strongly hydrated in solution show greater increase in conductivity with rise in temperature than salts that are slightly hydrated.

Aqueous solutions of organic acids were the subject of several investigations by Jones and his co-workers. White,³ while engaged in this work, found that the percentage temperature coefficients of conductivity of most of the organic acids examined were small, and decreased with rise in temperature and with increase in dilution. The rate of decrease of these coefficients, expressed in conductivity units, with rise in temperature, indicates that these acids are much less hydrated than mineral acids. In the case of the amino acids, the percentage coefficients of conductivity are very large. Internal salt formation was

¹Amer. Chem. Journ., **34**, 357 (1905).

²*Ibid.*, **40**, 355 (1908).

³*Ibid.*, **42**, 520 (1909).

suggested as the cause of these high values. He also shows that the conductivity of most organic acids is a parabolic function of the temperature, but concludes that no general statement can be made concerning the change in dissociation with temperature change, since the behavior of solutions of organic acid is not in accord with the Thompson-Nernst hypothesis connecting dissociating power and dielectric constant.

Clover¹ continued this work, but over a wider range of temperature. Some measurements were made at a temperature of 80°. West² and Wightman³ also did work in this field. The results obtained by these investigators were in accord with the findings of their predecessors.

Alum and other soluble salts were studied by Hosford and Jones. They found that the conductivity of an alum is less than the conductivity of the constituent salts. This is evidence in favor of a theory advanced by Jones regarding the existence of double salts, as such, in concentrated solutions.

While studying the conductivity of a number of electrolytes in aqueous solutions, Winston and Jones⁴ found apparent exceptions to the earlier work, viz, an increase in percentage dissociation with rise in temperature, and large temperature coefficients when there were no indications of large hydration. This led Winston to advance the theory that inductive action takes place through the solvent between charged ions and neutral molecules, giving rise to complex molecules and ions in solution.

Wightman,⁵ Springer,⁶ and Smith⁷ extended the work previously done in this laboratory on organic acids. The last-named investigator found that Euler's equation

$$\mu_t = \mu_0 + at - bt^2$$

holds in every case studied, and calls attention to the fact that isomeric acids do not behave similarly with regard to change in dissociation. That the migration velocity of anions is a function of the number of atoms constituting the anion was indicated by his experimental work.

Howard⁸ and Shaeffer⁹ have each published papers on conductivity work carried out under the direction of Jones.

In this brief review of the conductivity studies made in this laboratory, attention has been called to work done only on aqueous solutions. Similar work has been carried out by Jones and his collaborators, using glycerol, ethyl alcohol, and formamid as solvents. A considerable number of investigations involving various mixtures of different solvents have been carried out. For a full account of this work, Publications 80, 180, and 210 of the Carnegie Institution of Washington should be consulted.

¹Amer. Chem. Journ., **43**, 187 (1910).

²*Ibid.*, **44**, 508 (1910).

³*Ibid.*, **46**, 56 (1911).

⁴*Ibid.*, **46**, 368 (1911).

⁵*Ibid.*, **48**, 320 (1912).

⁶*Ibid.*, **48**, 411 (1912).

⁷*Ibid.*, **50**, 1 (1913).

⁸*Ibid.*, **48**, 500 (1912).

⁹*Ibid.*, **49**, 207 (1913).

EXPERIMENTAL.

APPARATUS.

Bridge and Rheostat.—All readings were made on an improved circular slide-wire bridge constructed by the Leeds and Northrop Co., of Philadelphia. From a bridge of this type, readings can be made to a fraction of a millimeter. The resistance-box had been recently standardized. The plugs of this piece of apparatus were kept clean by frequently rubbing them with a piece of soft chamois-skin moistened with alcohol.

Cells.—The cells used were of the same type described and sketched in previous articles¹ on this subject. Since all cells used had been in service for several years, no trouble was experienced from the leaching out of soluble constituents from the glass. On account of the rather wide range of conductivities shown by the salts studied, it was impossible, in every instance, to use the same cell for the same dilution.

Constant Temperature Baths.—With the exception of the zero bath, constant temperature was maintained by the application of a principle developed here by Morse.² This is best described in his own words:

“If all the water or air in a bath is made to pass *rapidly* (1) over a continuously cooled surface which is capable of reducing the temperature slightly below that which it is desired to maintain, then (2) over a heated surface which is more efficient than the cooled one, but under the control of a thermostat, and (3) again over the cooled surface, etc., it should be practicable to maintain in the bath any temperature for which the thermostat is set, and the constancy of the temperature should depend only on the sensitiveness of the thermostat and the rate of flow of the water or air. The principle is a general one and provides for the maintenance of any temperature between zero and the boiling-point of water.”

The particular type of bath and thermostat used was described fully by Davis and Putnam in Publication No. 210 of the Carnegie Institution of Washington. In making a zero bath of the type described by Jones and Jacobson,³ it was found necessary to reduce the ice to a fine state of division with an ice-shaver before a temperature of 0° could be obtained.

Containing Vessels.—All bottles and measuring flasks were of Jena glass. After recalibrating the flasks by the weight method, the flasks and the bottles were allowed to stand partly filled with a solution of chromic acid for several weeks. During this time they were frequently shaken to insure thorough cleansing.

SOLUTIONS.

Water.—The water used in the preparation of the solutions was purified by the method of Jones and MacKay⁴ as modified by Schmidt.⁵ In no case was the specific conductivity greater than 1.7×10^{-6} .

¹Carnegie Inst. Wash. Pub. No. 170, 6 (1912).

²*Ibid.*, 198, (1914).

³Amer. Chem. Journ., 40, 361 (1908).

⁴*Ibid.*, 19, 90 (1897).

⁵*Ibid.*, 17, 83 (1895).

Salts.—Kahlbaum's or Merck's best products were selected in all cases. These were recrystallized from conductivity water before being used.

Standardization.—On account of the nature of the substances studied, it was necessary to standardize most of the solutions by analytical methods. These methods will be taken up briefly in connection with the discussion of the individual salts. Standardization by analytical means is open to the objection that solutions must stand for some time before the conductivity measurements are made. This vitiates results in the case of salts which are hydrolyzed or undergo slight decomposition in solution. In the first instance alkali resulting from hydrolysis will attack the glass container, as was shown by the etching of a Jena glass bottle in which a N 8 solution of trisodiumphosphate had been standing for several weeks. By standardizing as rapidly as is consistent with accuracy, and by keeping the solutions in a cool, dark place, their deleterious effects are minimized. From the solution which had been analyzed, the others were made by diluting with conductivity water. Care was taken that no volume less than 35 c.c. should be involved in these measurements.

CELL CONSTANTS.

The cell constants were frequently determined throughout this work in the usual way, by means of a solution of pure potassium chloride. For the cells with electrodes some distance apart, a N/50 solution was used. The value found by Kohlrausch, 129.7 (Siemens units) at 25° was taken for the molecular conductivity of this solution. For the cells having their electrodes closer together, a N/500 solution was employed. The molecular conductivity of this had been determined in a cell the constant of which had been found by the use of the N/50 solution.

PRECAUTIONS.

Before proceeding to the experimental data and methods of calculating them, it may be well to call attention to a few precautions which, if taken, may assist those engaged in work requiring apparatus and methods somewhat similar to those used in this investigation.

(a) Jacobson¹ has already called attention to a method for the prevention of the collection of air-bubbles on the electrodes at 25° and above. He recommends heating the cell and contents a few degrees higher than the temperature at which the conductivity is to be measured, and then cooling them down to the desired temperature. In the light of Shaeffer's² work, it is seen that in the case of certain salts, notably chromium compounds, such treatment brings about a change in conductivity which persists for months. Shaeffer's observation was verified in the course of the present investigation. It was noticed that the conductivity of a solution of ammonium chromate was somewhat

¹Amer. Chem. Journ., **40**, 366 (1913).

²*Ibid.*, **49**, 240 (1908).

different at 25° after standing in the 25° bath, from the conductivity of the same solution when brought to a temperature of 25° from 0° to 15°. It was found best to remove the bubbles by tilting the cells slightly and partly removing the electrodes. If this is done once or twice while the solutions are coming to temperature, no further collection of bubbles will be noticed.

(b) The first few cubic centimeters of conductivity water should be discarded from the siphon used in drawing the water from its container. The water remaining below the stopcock is, to some extent, exposed to laboratory atmosphere, and if some time has elapsed since the removal of the last portion, considerable difference in conductivity will be noticed if the above precaution is neglected.

(c) All connections in the wiring system used with the conductivity apparatus should be soldered where this will not injure the apparatus. When not in use, the ends of the wires for connecting the cells with the bridge should be protected by small glass tubes.

(d) The noise of the motor used for stirring the baths was found to interfere with the reading of the bridge. This trouble was in a great measure overcome, by mounting the motor on heavy rubber sheeting, and providing washers of the same material for all bolts used in holding this machine in place.

RESULTS.

In tables 77 to 94 all conductivities are expressed in Siemens units, and are molecular conductivities—gram-molecular weights having been used in preparing the solutions. These molecular conductivities (μ_v) were calculated from the equation $\mu_v = K \frac{Va}{Rb}$, where K is the cell constant, V the volume concentration, R the resistance indicated on the rheostat, (a) and (b) the two arms of the bridge. The percentage dissociation (α) was calculated from the equation $\alpha = \frac{100\mu_v}{\mu_\infty}$, where μ_∞ is the highest value of μ_v obtained. The temperature coefficients expressed in conductivity units were calculated from the formula

$$\frac{(\mu_v)t_2 - (\mu_v)t_1}{t_2 - t_1} = \text{coefficient}$$

in which $(\mu_v)t_2$ represents μ_v at the higher temperature t_2 , and $(\mu_v)t_1$ at the lower temperature (t_1). The coefficients expressed as percentages were calculated from this formula

$$\frac{(\mu_v)t_2 - (\mu_v)t_1}{t_2 - t_1} \times \frac{100}{(\mu_v)t_1}$$

For every measurement shown in these tables three bridge readings involving different values for R were made, and the mean of these readings was taken as the basis of calculation.

SODIUM BROMATE.

This salt was twice recrystallized and then was dried at 100° for several hours; after cooling over phosphorus pentoxide, the required amount was weighed and dissolved. (See table 77.)

TABLE 77.—*Sodium bromate.*

V	Molecular conductivity.			Percentage dissociation.			Temperature coefficients.			
	0°	15°	25°	0°	15°	25°	0 to 15°		15 to 25°	
							<i>cond.</i> <i>units.</i>	<i>p. ct.</i>	<i>cond.</i> <i>units.</i>	<i>p. ct.</i>
8	42.77	63.62	78.84	69.9	74.4	74.8	1.38	3.22	1.52	2.39
16	44.94	67.03	83.38	73.5	78.4	79.1	1.47	3.27	1.63	2.43
32	47.49	70.72	87.95	77.7	82.7	83.5	1.54	3.24	1.72	2.43
128	49.64	74.39	92.67	81.2	87.0	88.0	1.64	3.30	1.82	2.45
512	52.69	78.76	96.53	86.2	92.1	91.6	1.73	3.28	1.77	2.25
1,024	53.10	79.59	99.26	86.9	93.1	94.2	1.76	3.31	1.96	2.47
2,048	58.27	85.45	105.1	95.3	100	99.5	1.81	3.10	1.97	2.30
4,096	61.10	83.34	105.3	100		100	1.48	2.42	2.19	2.63

SODIUM SULPHOCYANATE.

The original solution of this salt was standardized by treating a measured volume with a slight excess of an acidified solution of silver nitrate. The precipitate of silver sulphocyanate was filtered into a Gooch crucible, washed and weighed. Duplicate determinations were made as in the case of all solutions standardized by analysis. (See table 78.)

TABLE 78.—*Sodium sulphocyanate.*

V	Molecular conductivity.				Percentage dissociation.				Temperature coefficients.					
	0°	15°	25°	35°	0°	15°	25°	35°	0 to 15°		15 to 25°		25 to 35°	
									<i>cond.</i> <i>units.</i>	<i>p. ct.</i>	<i>cond.</i> <i>units.</i>	<i>p. ct.</i>	<i>cond.</i> <i>units.</i>	<i>p. ct.</i>
4	46.79	69.00	84.36	102.5	80.5	79.8	78.2	78.4	1.48	3.16	1.53	2.22	1.82	2.15
8	49.68	72.57	96.36	107.8	85.5	83.9	89.4	82.5	1.52	3.05	2.38	3.27	1.15	1.19
16	50.96	75.86	94.90	114.2	87.7	87.7	88.0	87.4	1.65	3.23	1.91	2.51	1.93	2.03
32	52.90	79.14	98.81	118.6	91.0	91.4	91.6	90.8	1.74	3.28	1.97	2.48	1.98	2.00
128	55.47	83.19	102.8	124.3	95.4	96.1	95.3	95.1	1.84	3.31	1.96	2.35	2.15	2.09
512	57.77	85.81	106.7	129.7	99.4	99.2	99.0	99.3	1.86	3.21	2.09	2.44	2.29	2.14
1,024	57.67	86.50	107.8	130.9	99.4	100	100	100	1.92	3.32	2.13	2.46	2.31	2.14
2,048	58.10	86.22	107.8	130.6	100				1.87	3.21	2.16	2.50	2.28	2.11

SODIUM THIOSULPHATE.

Iodine which had been resublimed in the presence of potassium iodide was weighed into small flasks with tightly fitting glass stoppers. About 2 gm. of potassium iodide and 0.5 c.c. of water had been previously weighed into these flasks. After the weight of the added iodine was determined, the flasks were opened in Erlenmeyer flasks containing 20 c.c. of water and potassium iodide. This solution was titrated with the thiosulphate. Starch solution was used as an indicator. (See table 79.)

SODIUM DITHIONATE.

After recrystallizing from conductivity water, 10 c.c. of the sodium dithionate solution was evaporated to dryness in a weighed platinum dish. After heating to dull redness for some time, the dish and contents were cooled over calcium chloride and weighed. From the weight of the sodium sulphate the strength of the original solution of sodium dithionate was calculated. (See table 80.)

SODIUM PYROPHOSPHATE.

This salt was dehydrated and weighed after it had been recrystallized. (See table 81.)

TRISODIUM PHOSPHATE.

All salts of orthophosphoric acid were treated in the same manner. After making a solution of approximately the required strength by weighing the salt, it was standardized by the method of Schmitz.¹

TABLE 79.—*Sodium thiosulphate.*

V	Molecular conductivity.				Percentage dissociation.				Temperature coefficients.					
	0°	15°	25°	35°	0°	15°	25°	35°	0 to 15°		15 to 25°		25 to 35°	
									cond. units.	p. ct.	cond. units.	p. ct.	cond. units.	p. ct.
4	77.90	115.3	143.3	172.6	59.2	59.1	58.7	59.4	2.49	3.07	2.80	2.43	2.93	2.04
8	82.52	129.8	160.8	196.0	62.8	66.5	65.9	67.4	3.15	3.81	3.10	2.38	3.52	2.18
16	94.10	143.4	178.4	214.8	71.6	73.5	73.1	73.9	3.28	3.48	3.50	2.44	3.64	2.04
32	103.0	153.2	193.0	235.0	78.4	78.5	79.1	80.8	3.34	3.24	3.98	2.60	4.19	2.17
128	113.1	172.4	214.9	259.9	86.0	88.4	88.0	89.4	3.95	3.49	4.24	2.46	4.50	2.09
512	126.0	189.0	234.0	283.8	95.8	96.9	95.9	97.6	4.19	3.32	4.50	2.38	4.98	2.12
1,024	124.8	191.9	239.1	284.1	94.9	98.4	97.9	97.7	4.47	3.58	4.70	2.45	4.50	1.88
2,048	128.1	194.1	241.1	284.3	97.5	99.5	98.8	97.8	4.40	3.43	4.69	2.41	4.32	1.79
4,096	131.4	195.0	244.0	290.5	100	100	100	100	4.23	3.22	4.90	2.50	4.65	1.90

TABLE 80.—*Sodium dithionate.*

V	Molecular conductivity.				Percentage dissociation.				Temperature coefficients.					
	0°	15°	25°	35°	0°	15°	25°	35°	0 to 15°		15 to 25°		25 to 35°	
									cond. units.	p. ct.	cond. units.	p. ct.	cond. units.	p. ct.
8	91.28	135.9	167.8	202.6	65.6	65.2	64.6	64.4	2.97	3.00	3.18	2.34	3.49	2.08
16	99.71	147.6	183.9	220.3	71.6	70.8	70.8	70.1	3.19	3.19	3.63	2.45	3.64	1.97
32	107.8	161.7	200.5	241.6	77.5	77.6	77.3	76.8	3.59	3.33	3.88	2.40	4.11	2.04
128	121.4	180.9	225.0	272.5	87.2	86.8	86.7	86.7	3.96	3.26	4.49	2.40	4.75	2.11
512	130.6	195.6	242.8	293.9	93.8	93.9	93.6	93.5	4.33	3.31	4.72	2.41	5.11	2.10
1,024	137.1	203.6	255.0	308.6	98.6	97.7	98.3	98.1	4.43	3.23	5.14	2.52	5.36	2.10
2,048	139.1	208.4	259.4	314.3	100	100	100	100	4.61	3.31	5.10	2.44	5.49	2.11
4,096	139.1	207.3	258.2	312.7					4.54	3.26	5.09	2.45	5.45	2.11

¹Zeit. anal. Chem., 45, 512 (1906).

This differs from the usual method, in that the magnesium ammonium phosphate is precipitated in a hot solution, by the slow addition of ammonia to an acid solution of the phosphate, to which an excess of "magnesia mixture" had been previously added. A very pure, coarsely crystalline precipitate, which settles readily, is obtained by this method. From the weight of the magnesium pyrophosphate yielded by this precipitate on ignition, the strength of the solution of the sodium salt was calculated. (See table 82.)

TABLE 81.—*Sodium pyrophosphate.*

V	Molecular conductivity.				Percentage dissociation.				Temperature coefficients.					
	0°	15°	25°	35°	0°	15°	25°	35°	0 to 15°		15 to 25°		25 to 35°	
									<i>cond.</i> <i>units.</i>	<i>p. ct.</i>	<i>cond.</i> <i>units.</i>	<i>p. ct.</i>	<i>cond.</i> <i>units.</i>	<i>p. ct.</i>
16	100.2	154.8	194.5	235.3	45.6	44.9	45.3	44.9	3.63	3.62	3.97	2.56	4.08	1.73
32	118.3	181.5	227.5	276.1	53.8	52.6	53.0	52.7	4.20	3.55	4.60	2.53	4.86	1.76
128	159.0	242.7	304.0	370.5	72.3	70.4	70.9	70.8	5.57	3.49	6.13	2.52	6.64	2.18
512	197.0	302.8	384.5	466.7	89.6	87.9	89.7	89.1	7.51	3.81	8.17	2.69	8.22	2.13
1,024	211.0	327.0	410.9	508.9	96.0	94.9	95.9	97.2	7.73	3.66	8.39	2.56	9.80	2.38
2,048	216.1	336.9	421.8	517.4	98.3	97.7	98.4	98.8	8.05	3.72	8.49	2.52	9.56	2.26
4,096	219.7	344.5	428.5	523.4	100	100	100	100	8.26	3.75	8.40	2.43	9.49	2.21

TABLE 82.—*Trisodium phosphate.*

V	Molecular conductivity.			Percentage dissociation.			Temperature coefficients.			
	0°	15°	25°	0°	15°	25°	0 to 15°		15 to 25°	
							<i>cond.</i> <i>units.</i>	<i>p. ct.</i>	<i>cond.</i> <i>units.</i>	<i>p. ct.</i>
32	120.5	195.3	254.2	61.5	63.6	66.8	4.98	4.13	5.89	3.01
128	163.7	261.7	338.1	83.6	85.2	88.8	6.53	3.98	7.64	2.91
512	185.2	292.8	361.5	94.6	95.3	95.0	7.17	3.87	6.86	2.34
1,024	195.8	307.0	380.5	100	100	100	7.41	3.79	7.35	2.39

TABLE 83.—*Sodium dihydrogen phosphate.*

V	Molecular conductivity.				Percentage dissociation.				Temperature coefficients.					
	0°	15°	25°	35°	0°	15°	25°	35°	0 to 15°		15 to 25°		25 to 35°	
									<i>cond.</i> <i>units.</i>	<i>p. ct.</i>	<i>cond.</i> <i>units.</i>	<i>p. ct.</i>	<i>cond.</i> <i>units.</i>	<i>p. ct.</i>
8	31.02	47.47	59.79	72.40	72.2	72.4	73.2	71.9	1.09	3.52	1.23	2.59	1.26	2.10
16	33.75	51.62	64.45	79.55	78.5	78.7	78.9	79.0	1.19	3.52	1.28	2.48	1.51	2.34
32	36.16	55.24	69.25	84.25	84.2	84.3	84.8	83.7	1.27	3.51	1.40	2.53	1.50	2.16
128	40.13	60.98	75.39	93.67	93.4	93.0	94.7	93.1	1.38	3.43	1.44	2.36	1.80	2.42
512	43.00	65.52	81.59	99.90	100	100	100	99.3	1.50	3.46	1.60	2.45	1.83	2.24
1,024	42.07	64.95	81.17	100.6				100	1.52	3.55	1.62	2.48	1.94	2.39

SODIUM DIHYDROGEN PHOSPHATE.

The solution of this salt was standardized by the method discussed in connection with the trisodium phosphate. (See table 83.)

SODIUM TUNGSTATE.

The original solution of sodium tungstate was standardized by precipitating the tungstic acid as mercurous tungstate. On ignition, this yields the trioxide of tungsten, which can be weighed. (See table 84.)

SODIUM FORMATE.

In a cold acid solution, permanganate acts only slowly with formic acid, while in a hot solution the latter is lost by volatilization. In spite of statements to the contrary, oxidation by means of permanganate in an alkaline solution is a most unsatisfactory process. This led to the use of an indirect method of standardization for the sodium formate solution. An excess of standard permanganate solution was measured from a burette into an alkaline solution of the formate. After standing

TABLE 84.—*Sodium tungstate.*

V	Molecular conductivity.				Percentage dissociation.				Temperature coefficients.					
	0°	15°	25°	35°	0°	15°	25°	35°	0 to 15°		15 to 25°		25 to 35°	
									cond. units.	p. ct.	cond. units.	p. ct.	cond. units.	p. ct.
4	59.56	100.2			54.8	59.9			2.71	4.55				
8	69.75	112.7	141.6	172.0	64.2	67.3	66.9	67.3	2.86	4.10	2.88	2.56	3.24	2.28
16	82.65	126.7	159.0	193.2	76.1	75.7	75.2	75.7	2.93	3.54	3.23	2.54	3.42	2.15
32	87.53	134.3	168.7	205.5	80.6	80.3	79.8	80.5	3.12	3.56	3.44	2.56	3.68	2.18
128	98.54	151.5	190.7	233.5	90.7	90.5	90.2	91.4	3.52	3.57	3.92	2.58	4.28	2.24
512	107.25	164.6	207.4	254.1	98.7	98.3	98.1	99.5	3.82	3.56	4.28	2.60	4.67	2.25
1,024	108.67	167.3	211.4	255.2	100	100	100	100	3.90	3.56	4.41	2.63	4.38	2.07

TABLE 85.—*Sodium formate.*

V	Molecular conductivity.				Percentage dissociation.				Temperature coefficients.					
	0°	15°	25°	35°	0°	15°	25°	35°	0 to 15°		15 to 25°		25 to 35°	
									cond. units.	p. ct.	cond. units.	p. ct.	cond. units.	p. ct.
4	56.09	84.34	105.0	126.4	70.3	71.0	70.9	68.6	1.88	3.35	2.07	2.45	2.14	2.03
8	62.13	91.91	113.6	140.1	77.9	77.4	76.7	76.0	1.84	2.96	2.16	2.35	2.65	2.33
16	64.75	97.82	121.4	147.4	81.2	82.4	81.9	80.0	1.53	2.36	2.35	2.41	2.60	2.14
32	67.72	99.10	130.2	157.1	84.9	83.5	87.9	85.3	2.09	3.08	3.11	3.13	2.69	2.00
128	72.48	109.8	137.7	166.3	90.9	92.5	92.9	90.3	2.48	3.42	2.80	2.55	2.86	2.07
512	74.63	109.6	139.1	166.7	93.6	92.4	93.9	90.5	2.35	3.14	2.95	2.69	2.76	1.99
1,024	75.65	112.8	140.9	181.0	94.8	95.0	95.1	98.3	2.47	3.26	2.81	2.49	4.01	2.84
2,048	78.68	114.8	147.9	184.7	98.7	96.7	99.8	100	2.41	3.06	3.31	2.88	3.68	2.49
4,096	79.73	118.7	148.1	184.1	100	100	100		2.59	3.24	2.94	2.49	3.60	2.43

for some time, a known weight of pure sodium oxalate was added. The solution was then acidified and heated. A standard solution of permanganate was used to titrate this in the usual way. The total amount of permanganate less that which is equivalent to the sodium oxalate is the permanganate used for the oxidation of the sodium formate. (See table 85.)

SODIUM CHROMATE.

The original solution of this salt was standardized by precipitating the chromium as mercurous chromate, by means of a solution of mercurous nitrate. On ignition, the mercurous chromate leaves a residue of chromic oxide which can be weighed. (See table 86.)

SODIUM DICHROMATE.

The same method of standardization was used in the case of sodium dichromate as was employed with the chromate. (See table 87.)

POTASSIUM FERRICYANIDE.

This salt was dried for more than a month over phosphorus pentoxide. The solution was prepared by weighing the required amount of the dry salt, and dissolving in the usual manner. (See table 88.)

TABLE 86.—*Sodium chromate.*

V	Molecular conductivity.				Percentage dissociation.				Temperature coefficients.					
	0°	15°	25°	35°	0°	15°	25°	35°	0 to 15°		15 to 25°		25 to 35°	
									cond. units.	p. ct.	cond. units.	p. ct.	cond. units.	p. ct.
4	74.76	113.4			63.2	64.3			2.57	3.43				
8	83.56	125.3	156.5	187.9	70.6	71.1	71.3	69.6	2.78	3.32	3.12	2.48	3.14	2.00
16	90.74	137.8	171.3	207.6	76.7	78.2	78.0	76.8	3.13	3.44	3.35	2.43	3.63	2.11
32	98.16	148.6	185.1	224.3	82.9	84.3	84.3	83.0	3.36	3.42	3.65	2.45	3.92	2.11
128	110.40	168.4	206.7	252.2	93.3	95.5	94.2	93.4	3.86	3.49	3.83	2.27	4.55	2.20
512	118.32	176.2	219.5	270.1	100	100	100	100	3.85	3.25	4.33	2.45	5.06	2.30
1,024	114.60	173.6	216.9	262.3					3.92	3.42	4.33	2.49	4.54	2.09

TABLE 87.—*Sodium dichromate.*

V	Molecular conductivity.				Percentage dissociation.				Temperature coefficients.					
	0°	15°	25°	35°	0°	15°	25°	35°	0 to 15°		15 to 25°		25 to 35°	
									cond. units.	p. ct.	cond. units.	p. ct.	cond. units.	p. ct.
8	92.18	136.5			87.2	86.22			2.95	3.20				
16	96.57	143.5	176.3	211.4	91.3	90.65	90.71	89.88	3.13	3.24	3.28	2.28	3.51	1.99
32	101.25	148.4	182.7	219.5	95.7	93.74	93.98	93.32	3.14	3.10	3.43	2.31	3.68	2.01
128	106.8	158.3	194.7	233.5	100	100	100	100	3.43	3.21	3.64	2.29	3.88	1.99
512	106.1	158.3	194.4	234.6					3.50	3.31	3.61	2.28	4.02	2.06

AMMONIUM IODATE.

A very dilute solution of the iodate, while cold, was carefully treated with sulphurous acid. When an amount sufficient to remove the brown color due to free iodine had been added, the solution was warmed until the odor of sulphur dioxide could not be detected. The iodine was then determined as silver iodide. (See table 89.)

TABLE 88.—*Potassium ferricyanide.*

V	Molecular conductivity.				Temperature coefficients.					
	0°	15°	25°	35°	0 to 15°		15 to 25°		25 to 35°	
					cond. units.	p. ct.	cond. units.	p. ct.	cond. units.	p. ct.
8	158.6	230.2	282.1		4.77	3.00	5.19	2.25		
16	168.8	247.3	303.3	360.1	5.23	3.09	5.60	2.26	5.68	1.87
32	181.4	266.4	326.4	389.3	5.66	3.11	6.00	2.25	6.29	1.92
128	207.4	308.2	380.1	451.7	6.71	3.23	7.19	2.33	7.16	1.88
512	229.2	331.8	410.1	494.5	6.83	2.98	7.87	2.37	8.40	2.04
1,024	238.1	354.5	438.9	529.9	7.75	3.25	8.44	2.37	9.10	2.07
2,048	244.4	363.0	449.5	543.3	7.90	3.23	8.65	2.38	9.38	2.08
4,096	254.5	375.3	465.8	564.3	8.05	3.16	9.04	2.40	9.86	2.11

TABLE 89.—*Ammonium iodate.*

V	Molecular conductivity.				Percentage dissociation.				Temperature coefficients.					
	0°	15°	25°	35°	0°	15°	25°	35°	0 to 15°		15 to 25°		25 to 35°	
									cond. units.	p. ct.	cond. units.	p. ct.	cond. units.	p. ct.
16	48.17	72.21	89.97	108.5	85.1	84.88	84.7	84.4	1.60	3.32	1.77	2.45	1.85	2.05
32	50.51	76.35	94.93	114.6	89.2	89.74	89.4	89.1	1.72	3.40	1.85	2.43	1.97	2.07
128	54.34	81.32	101.1	122.2	96.0	95.59	95.2	95.0	1.79	3.29	1.97	2.43	2.11	2.08
512	56.54	85.07	106.2	128.6	99.9	100	100	100	1.90	3.35	2.12	2.49	2.24	2.10
1,024	56.60	84.93	105.9	128.0	100				1.88	3.32	2.10	2.47	2.21	2.08
2,048	55.99	83.92	104.6	127.2					1.86	3.32	2.07	2.46	2.26	2.16

TABLE 90.—*Ammonium dihydrogen phosphate.*

V	Molecular conductivity.				Percentage dissociation.				Temperature coefficients.					
	0°	15°	25°	35°	0°	15°	25°	35°	0 to 15°		15 to 25°		25 to 35°	
									cond. units.	p. ct.	cond. units.	p. ct.	cond. units.	p. ct.
4	37.56	56.27	69.66	83.53	66.4	67.0	66.5	65.9	1.24	3.30	1.34	2.37	1.38	1.98
8	41.18	61.73	76.50	92.71	72.8	73.5	73.1	73.1	1.36	3.30	1.47	2.39	1.62	2.11
16	44.45	66.55	82.57	99.90	78.6	79.3	78.9	78.8	1.47	3.30	1.60	2.40	1.73	2.09
32	46.72	70.65	87.73	106.48	82.6	84.1	83.8	84.0	1.59	3.40	1.70	2.41	1.87	2.13
128	50.74	76.21	94.89	114.75	89.8	90.8	90.7	90.5	1.69	3.33	1.86	2.45	1.98	2.09
512	53.39	81.01	99.73	121.2	94.5	96.5	95.3	95.6	1.83	3.42	1.87	2.31	2.15	2.15
1,024	56.50	83.92	104.6	126.7	100	100	100	100	1.83	3.23	2.07	2.46	2.21	2.11

AMMONIUM DIHYDROGEN PHOSPHATE.

This solution was standardized in the same way as described in connection with sodium phosphate. (See table 90.)

AMMONIUM CHROMATE.

The method used for standardization was identical with that employed for standardizing the chromate of sodium. (See table 91.)

TABLE 91.—*Ammonium chromate.*

V	Molecular conductivity.				Percentage dissociation.				Temperature coefficients.					
	0°	15°	25°	35°	0°	15°	25°	35°	0 to 15°		15 to 25°		25 to 35°	
									cond. units.	p. ct.	cond. units.	p. ct.	cond. units.	p. ct.
4	93.63	137.0			64.7	64.2			2.89	3.08				
8	102.5	149.8	181.9	215.4	70.8	70.3	69.3	68.8	3.15	3.07	3.21	2.14	3.35	1.88
16	110.5	163.1	199.5	236.7	76.4	76.5	76.0	75.7	3.50	3.16	3.64	2.23	3.72	1.89
32	119.1	176.3	215.4	257.2	82.3	82.7	82.1	82.2	3.81	3.19	3.91	2.21	4.18	1.94
128	135.1	201.2	247.1	292.7	93.4	94.3	94.2	93.6	4.40	3.25	4.59	2.28	4.56	1.84
512	144.6	213.2	262.2	312.7	100	100	100	100	4.57	3.16	4.90	2.29	4.95	1.88
1,024	143.0	212.6	261.7	312.3					4.63	3.23	4.91	2.30	5.06	1.93

TABLE 92.—*Ammonium sulphocyanate.*

V	Molecular conductivity.				Percentage dissociation.				Temperature coefficients.					
	0°	15°	25°	35°	0°	15°	25°	35°	0 to 15°		15 to 25°		25 to 35°	
									cond. units.	p. ct.	cond. units.	p. ct.	cond. units.	p. ct.
4	60.46	86.53	106.0	125.7	83.9	82.2	82.0	81.2	1.73	2.86	2.05	2.37	1.97	1.89
8	61.47	89.84	110.3	131.7	85.3	85.3	85.3	85.0	1.89	3.07	2.04	2.27	2.14	1.94
16	63.58	93.60	114.4	137.5	88.3	88.9	88.5	88.8	2.00	3.14	2.08	2.22	2.31	2.01
32	66.30	97.48	119.5	143.4	92.0	92.6	92.5	92.6	2.07	3.12	2.20	2.26	2.39	2.00
128	68.58	101.2	124.2	148.9	95.2	96.2	96.1	96.2	2.17	3.16	2.29	2.26	2.47	1.99
512	71.74	105.2	129.0	154.5	99.6	100	99.8	99.8	2.23	3.10	2.48	2.35	2.55	1.97
1,024	72.00	105.2	129.2	154.8	100		100	100	2.21	3.06	2.40	2.28	2.56	1.97

TABLE 93.—*Lithium chromate.*

V	Molecular conductivity.				Percentage dissociation.				Temperature coefficients.					
	0°	15°	25°	35°	0°	15°	25°	35°	0 to 15°		15 to 25°		25 to 35°	
									cond. units.	p. ct.	cond. units.	p. ct.	cond. units.	p. ct.
8	74.62	112.3	139.9	169.1	65.4	67.3	66.9	67.2	2.51	3.36	2.76	2.45	2.92	2.08
16	82.62	124.1	154.3	187.3	72.4	74.3	73.8	74.5	2.76	3.34	3.02	2.45	3.30	2.13
32	89.83	136.6	169.9	205.5	78.7	81.8	81.3	81.7	3.11	3.46	3.33	2.43	3.56	2.09
128	101.6	155.1	193.0	236.5	89.0	92.9	92.3	94.0	3.56	3.50	3.79	2.44	3.34	1.73
512	106.4	164.5	205.3	249.0	93.2	98.5	98.2	99.0	3.87	3.60	4.08	2.48	4.37	2.12
1,024	108.1	166.0	206.2	250.3	94.7	99.4	98.6	99.5	3.85	3.59	4.02	2.42	4.41	2.13
2,048	114.1	168.3	209.0	251.4	100	100	100	100	3.61	3.16	4.07	2.41	4.24	2.02

AMMONIUM SULPHOCYANATE.

The amount of sulphocyanate present in the original solution was found by weighing the silver sulphocyanate formed on treating a portion of the solution with silver nitrate. (See table 92.)

LITHIUM CHROMATE.

The chromate in this solution was determined as it was in the case of sodium chromate. (See table 93.)

RUBIDIUM IODIDE.

The iodine was determined as silver iodide. (See table 94.)

TABLE 94.—*Rubidium iodide.*

V	Molecular conductivity.				Percentage dissociation.				Temperature coefficients.					
	0°	15°	25°	35°	0°	15°	25°	35°	0 to 15°		15 to 25°		25 to 35°	
									cond. units.	p. ct.	cond. units.	p. ct.	cond. units.	p. ct.
4	68.40	97.08			85.41	82.9			1.91	2.79				
8	70.48	101.4	122.6	145.6	88.0	86.6	85.6	85.2	2.06	2.92	2.01	1.98	2.30	1.87
16	72.59	104.3	127.2	150.6	90.6	89.0	88.8	88.1	2.11	2.90	2.29	2.19	2.34	1.83
32	74.75	108.6	131.7	157.8	93.3	92.7	92.0	92.3	2.25	3.01	2.31	2.12	2.61	1.98
128	78.51	114.2	139.7	166.6	98.0	97.5	97.6	97.5	2.38	3.03	3.57	3.12	2.69	1.92
512	79.92	116.0	142.0	169.5	99.8	99.0	99.2	99.2	2.40	3.00	3.60	3.11	2.75	1.93
1,024	80.08	117.1	143.1	170.8	100	100	100	100	2.46	3.07	3.70	3.16	2.77	1.93

DISCUSSION OF RESULTS.

CONDUCTIVITIES.

Electrical conductivity in solutions of electrolytes depends on the number of ions present and on the velocities of these ions. The velocities, other conditions being the same, depend upon the size and mass of the ion and upon the viscosity of the medium. This leads to the conclusion that a salt showing a high conductivity must be dissociated into a great number of ions, or the ions in solutions must be of such a size and mass that they have a great velocity.

It can be seen from the above tables that certain salts, notably trisodium phosphate, sodium pyrophosphate, ammonium chromate, and potassium ferricyanide, show very high conductivity. The first of these compounds is strongly hydrolyzed even at low temperatures. The breaking down of complexes by hydrolysis gives rise to a great number of ions also in the case of the pyrophosphate. It is interesting to compare the conductivity of the trisodium phosphate with that of the corresponding potassium compound. While both show very high conductivities at all temperatures, the conductivity of the potassium salt is greater than that of the sodium. We would expect this from

the fact that the sodium salt crystallizes with 12 molecules of water, indicating great hydration in solution; while the potassium salt has no water of crystallization, which indicates only slightly hydrated ions in solution. The ammonium chromate is somewhat similar to the unhydrated potassium salt mentioned above, in that it carries no water of crystallization, and would therefore be expected to show greater conductivity than the corresponding hydrated salts of sodium and lithium. The high values of μ for potassium ferri-cyanide is largely due to the great number of ions yielded by this compound. The work of Getman and Bassett¹ indicates the production of 6 ions in solutions of this salt. By comparing the conductivities of the chromates of ammonia and the alkali metals, it is found that they stand in the following order:

Potassium chromate > ammonium chromate > sodium chromate > lithium chromate.

Ammonium compounds, as a rule, show higher conductivity than the corresponding potassium salts. This does not seem to be true in the case of the chromates. The smaller conductivities of lithium compounds when compared with compounds of sodium, is usually attributed to the greater hydration of the lithium ion in solution, as indicated by the greater tendency of lithium salts to crystallize with water.¹ The chromate of lithium, however, crystallizes with 1 molecule of water, while the chromate of sodium contains 10 molecules. The work of Jones and Bassett² has shown that many substances have greater hydrating power than is indicated by the water of crystallization contained in them. Such may be the case with lithium chromate.

Rubidium iodide shows a higher conductivity than the iodides of the other alkali metals. Knowing that rubidium has a greater atomic volume than sodium or potassium, we might expect the conductivity to be lowered by a decrease in the velocity of the ions, due to their volume and mass. It should, however, be remembered that the hydrating power of these compounds of the alkali metals decreases with increasing atomic volume. Just as sodium salts are less hydrated than lithium, so rubidium compounds would be expected to hydrate less than potassium. Thus, an apparent exception is explained by the theory of hydration.

DISSOCIATIONS.

As a means of determining the dissociation of salts in solution, the conductivity method is of great service, but it is far from perfect. Hydrolysis, hydration, and polymerization all militate against obtaining a true value for μ_{∞} . Since most salts show one or more of the above-named phenomena, it is certain that dissociations calculated from conductivity data are in most cases simply close approximations.

¹Carnegie Inst. Wash. Pub. No. 60, p. 46 (1907).

²Amer. Chem. Journ., 33, 562 (1905).

As a rule, salts in aqueous solutions are more dissociated at low than at high temperatures. This is in accord with the Thompson-Nernst hypothesis to which reference has already been made. Some exceptions to this rule have been found by other investigators. Barium nitrate, cadmium iodide, lead nitrate, and uranyl acetate have been found to show an increase in dissociation at higher temperatures. Shaeffer¹ has called special attention to the anomalous behavior of tripotassium phosphate, and suggests as a cause abnormal exothermic heat of dissociation. A great number of the substances studied in the present investigation showed a slight decrease in dissociation with rise in temperature. Sodium bromate, sodium thiosulphate, trisodium phosphate, and lithium chromate showed a well-defined increase. Several compounds have almost identical dissociations at all the temperatures studied.

TEMPERATURE COEFFICIENTS.

It has been found that the increase in conductivity with rise in temperature, is due primarily to the velocities with which the ions move. This velocity is governed by the viscosity of the medium and the volume and mass of the ion. It is well known that the general tendency of rise in temperature is to decrease viscosity, and also the volume and mass of the ion, if the ion is considered not as a charged atom or group of atoms, but as a charged nucleus plus molecules of water, which must be carried along in all migrations through the remainder of the solvent. Jones has given a number of proofs for the validity of this conception of ions. He has also shown that these complexes break down at higher temperatures. With these facts in mind, we should expect a greater increase in conductivity with rise in temperature in the case of strongly hydrated salts than in the case of weakly hydrated substances. Taking the amount of water with which a substance crystallizes as indicative of the extent to which it is hydrated, it is found that all of the compounds referred to in the above tables are in accord with this conception, except potassium ferricyanide and ammonium chromate. Reference has been made to the work of Jones and Getman and Jones and Bassett, which throws some light on the dissociation of the complex ferricyanide, and also shows that water of crystallization is not always indicative of the degree of hydration to which a compound is subject. While they proved that the ferricyanide is not hydrated, it is rather probable that the lithium chromate is, since lithium salts, as a class, have a much greater tendency to hydrate than the salts of sodium or potassium.

The temperature coefficients, expressed in percentage, decrease in each case with rise in temperature. They increase somewhat on dilution. This is especially noticeable with hydrated and hydrolyzed salts.

¹Amer. Chem. Journ., 49, 249 (1913).

Jones¹ has pointed out the following general relations deduced from the study of a large number of data concerning temperature coefficients:

1. Those ions with the largest hydrating power have the largest temperature coefficients of conductivity.

2. Those substances having equal hydrating power have approximately the same temperature coefficients of conductivity.

3. At higher dilutions, the temperature coefficients of conductivity, for any given substance, are greater than at lower dilutions.

In the present investigation all of these relations have been found to hold, with the few apparent exceptions noted in the above discussion.

SUMMARY.

1. A brief sketch of the work done in this laboratory on the conductivity of aqueous solutions, together with a résumé of the results obtained by Jones and his co-workers, has been given.

2. A few practical suggestions as to apparatus and methods of procedure are offered.

3. Eighteen more or less unusual salts were studied with reference to their conductivity, over a range of temperature from 0° to 35°. Their temperature coefficients of conductivity are expressed in two sets of units; and where it is possible their dissociation has been calculated.

4. The results of this investigation are, for the most part, in accord with the findings of other workers in this field. Three exceptions were found to the rule that dissociation decreases with rise in temperature. Two apparent exceptions to the rule that large temperature coefficients of conductivity are indicative of great hydration are noted and possible explanations are offered.

¹Amer. Chem. Journ., **34**, 357 (1905).

CHAPTER IX.

THE DISSOCIATING POWERS OF FREE AND OF COMBINED WATER.

By G. FRED. ORDEMAN.

INTRODUCTION.

One of the most interesting and important results established by Jones and Guy,¹ in their work with the radiomicrometer on the absorption spectra of solutions, was the effect of the dissolved substance on the absorption spectra of water. They noted that aqueous solutions of hydrated salts were often more transparent than pure water. The absorption of aqueous solutions of strongly hydrated salts was compared by them with the absorption of a layer of water equal in depth to the water in the solution. Similar experiments were carried out with salts which were but slightly hydrated. The concentrated solutions of strongly hydrated salts, *e. g.*, 5.3-normal solution of calcium chloride, were found to be more transparent than a comparable quantity of pure water. In the case cited, the transparency was 25 per cent greater from 1.05μ to 1.2μ . The solutions of slightly hydrated salts, *e. g.*, potassium chloride, ammonium chloride, and ammonium nitrate, were found to have, in general, the same absorption as water having the same depth as the water in the solution. To account for the facts, they concluded that the combined water has less power to absorb light than free or uncombined water. This is regarded by them as striking evidence that some of the water in the presence of salts which by other methods are shown to hydrate, is different from pure, free, uncombined water. The simplest explanation seems to be that this is combined water or water of hydration.

The work of Jones and Guy has been repeated and extended by Jones, Shaeffer, and Paulus.² Their results are of the same general character. In some instances they found the aqueous solutions of hydrated salts to be 40 per cent more transparent than a comparable quantity of pure water.

Believing a determination of the power of dissociation of combined water might aid in explaining the above facts, Dr. Shaeffer suggested the use of isochloric solutions in the manner we have adopted. The object of this work has been to ascertain the difference, if any, between the dissociating power of combined water or water of hydration, and the dissociating power of uncombined or free water.

¹Carnegie Inst. Wash. Pub. No. 190 (1913). Phys. Zeit., 14, 278 (1913).

²*Ibid.*, 210 (1915).

EXPERIMENTAL APPARATUS.

The Kohlrausch method of measuring conductivity was employed with Wheatstone bridge, telephone receiver, and induction coil. A full description of the apparatus and the method of its use may be found in the earlier publications of work from this laboratory.

Because of the concentrated solutions employed, a different type of cell was necessary. This consisted of a hard-glass, U-shaped tube, fitted with ground-glass stoppers. The glass tubes carrying the electrodes were sealed by means of sealing-wax into the holes bored in the centers of the stoppers. The distance between the electrodes could thus be adjusted if occasion demanded. Numbers were etched upon the stoppers and the corresponding arms of the U-tubes, so that the electrodes could always be placed in the same position.

The temperature was very satisfactorily maintained by means of a new thermostat described in detail by Jones, Davis, and Putnam.¹

All flasks and burettes were carefully calibrated. Solvent and solutions in all cases were brought to within 0.1° of the necessary temperature before measurements were made.

SOLVENTS.

WATER.

The water was purified by the method of Jones and MacKay² as modified by Schmidt, and had a mean specific conductivity of 1.5×10^{-6} at 25° C.

ISOCHLORIC SOLUTIONS.

Two solutions are said to be isochloric if they contain in unit volume the same number of chlorine ions. In this work we have used a solution of potassium chloride normal at 25°, and the solution of calcium chloride with which this would be isochloric.

Arrhenius³ shows, for the condition of isohydric solutions

$$\frac{ma}{v_1} = \frac{n\beta}{v_2} \quad (1)$$

Applying this to the solutions under discussion:

α = percentage dissociation of normal solution of potassium chloride;

β = that of the corresponding solution of calcium chloride.

Let v_1 = liters of solution containing a gram-molecular weight of potassium chloride and v_2 = corresponding symbol for the calcium chloride.

Let m = number of chlorine ions per molecule of potassium chloride and n = same for calcium chloride.

¹Carnegie Inst. Wash. Pub. No. 210, 119 (1915).

²Amer. Chem. Journ., 17, 83 (1895).

³Zeit. phys. Chem. 2, 284 (1886).

In calculating the percentage dissociations by the conductivity method—

$$\alpha = \frac{\mu_1}{\mu_{1\infty}} \quad \beta = \frac{\mu_2}{\mu_{2\infty}} \quad (2)$$

Here μ_1 = molecular conductivity of the solution of potassium chloride, and μ_2 = that of the solution of calcium chloride. Further, $\mu_{1\infty}$ = conductivity at infinite dilution for the potassium chloride and $\mu_{2\infty}$ = same for calcium chloride.

From the method of Kohlrausch for calculating conductivity,

$$\mu_1 = K_1 \frac{a_1 v_1}{b_1 w_1} \quad \mu_2 = K_2 \frac{a_2 v_2}{b_2 w_2} \quad (3)$$

K_1 and K_2 are cell constants. a_1 , b_1 , a_2 , and b_2 are readings on the bridge for the corresponding resistances.

Substituting the values of (3) in (2) we obtain

$$\alpha = \frac{K_1 a_1 v_1}{b_1 w_1 \mu_{1\infty}} \quad \text{and} \quad \beta = \frac{K_2 a_2 v_2}{b_2 w_2 \mu_{2\infty}} \quad (4)$$

Substituting these values in (1)

$$\frac{m K_1 a_1 v_1}{b_1 w_1 \mu_{1\infty} v_1} = \frac{n K_2 a_2 v_2}{b_2 w_2 \mu_{2\infty} v_2}$$

For potassium chloride $m = 1$ and for calcium chloride $n = 2$. If the same cell be used then $K_1 = K_2$. And

$$\frac{a_1}{b_1 w_1 \mu_{1\infty}} = \frac{2a_2}{b_2 w_2 \mu_{2\infty}}$$

At 25° $\mu_{1\infty} = 137^1$ and $\mu_{2\infty} = 246.5$.

Therefore,

$$\frac{a_1}{137 b_1 w_1} = \frac{2a_2}{246.5 b_2 w_2} \quad (5)$$

Whence,

$$0.8996 \times \frac{a_1}{b_1 w_1} = \frac{a_2}{b_2 w_2}$$

Now, by measuring a and b of the solution of potassium chloride for the resistance w_1 , the left-hand side of the equation becomes a constant. A concentrated solution of calcium chloride is now taken in different portions and diluted in different amounts until $\frac{a_2}{b_2 w_2}$ becomes equal to the value for the left-hand side.

The conductivity of the potassium chloride solution was found to be 103.6. The specific conductivity of the calcium chloride solution was found to be 93.12. The calcium chloride solution upon analysis proved to be 0.6951 molar.

¹Carnegie Inst. Wash. Pub. No. 170, p. 20 (1912).

SALTS.

The sodium chloride, potassium chloride, and ammonium chloride were the best grade of Baker's analyzed chemicals. These salts were carefully recrystallized from conductivity water and thoroughly dried. The calcium chloride, magnesium chloride, and strontium chloride were from Eimer and Amend. These were dissolved in conductivity water and filtered. They were not recrystallized, being so soluble, but, as later described, were used as concentrated solutions.

SOLUTIONS.

Solutions of the non-hydrated salts were made by dissolving the requisite weights of salt in the two isochloric solutions and diluting to the mark with these two solutions. It was found that the volume change caused by the added salts was very considerable in the more concentrated solutions. This means that the solutions, when made, would be of the proper strength for the added salts, but weaker for the isochloric solutions. Part of the space occupied by the isochloric solutions is now taken by the added salt. However, the change in volume in the two isochloric solutions was the same for the same added salt. This would still allow the results to be comparable, even though no correction had been made for the volume change.

Solutions of the hydrated salts were made by using the quantities of a concentrated solution of known strength necessary for the normality desired. Instead of using isochloric solutions, the necessary amounts of potassium chloride and of a concentrated solution of calcium chloride were employed. The solutions were now brought to the calibration mark by conductivity water. In this way a solution was obtained accurate with respect to the isochloric solution as well as to the added salt. The strengths of the various concentrated solutions were determined by an estimation of the chlorine as silver chloride. The analyses were, of course, made in duplicate. All solutions were made up at 25° C. The same flask was used for normal solutions throughout. This was likewise done for half-normal and eighth-normal solutions.

PROCEDURE.

The specific conductivities of the two solutions which were isochloric were first measured and computed from the formula $s = K \frac{a}{wb}$. The same cell was employed for both solutions, so that any change in the cell constant or any error in its determination would be eliminated for comparison.

Solutions were made in the manner described, which were isochloric with regard to the potassium chloride and calcium chloride, but which were also of a known normality for an added salt. The specific con-

ductivities of these solutions were now determined. These were not the sum of the specific conductivities of the two salts present in each case, but were less, because of the common ion effect. But since the two solutions contain the same number of ions (the added salt not being considered), the driving back of the dissociation of the added salt by the anions would be the same in each case. When the conductivity of a solution, say, normal with respect to potassium chloride and half normal with respect to magnesium chloride, had been measured, the cell was thoroughly cleaned and dried. This same cell was now used for the determination of the conductivity of a solution 0.6951 normal with respect to calcium chloride, that is, isochloric, and half-normal as regards magnesium chloride. Thus the possibility of error due to any change in the cell was eliminated.

Three concentrations of the added salt were used, first in solutions normal for potassium chloride and then in solutions 0.6957 normal for calcium chloride. The increase in conductivity due to the added salt was calculated in each case. The difference of the increases for comparable solutions was then computed.

The numbers given here for conductivities represent the mean of three readings of the bridge for different resistances.

TABLE 95.
Normal for KCl. 0.6951 normal for CaCl₂.

Added salt.	Specific conductivity.	Increase over S of mKCl.	Specific conductivity.	Increase over S of 0.6951m CaCl ₂ .	Difference in increases.
NaCl 8	111.78	8.18	100.57	7.45	0.73
NaCl 2	135.78	32.18	120.33	27.21	4.97
NaCl 1	162.09	58.49	142.67	49.55	8.94
KCl 8	115.38	11.78	103.35	10.23	1.55
KCl 2	148.75	45.15	132.56	39.44	5.71
KCl 1	191.68	88.08	169.98	76.86	11.22
NH ₄ Cl 8	115.30	11.70	103.25	10.13	1.57
NH ₄ Cl 2	148.25	44.65	132.06	38.84	5.81
NH ₄ Cl 1	190.14	86.54	169.98	76.86	9.68
MgCl ₂ 8	117.02	13.42	104.03	10.91	2.51
MgCl ₂ 2	148.11	44.51	131.38	38.26	6.25
MgCl ₂ 1	174.54	70.94	148.83	55.71	15.23
CaCl ₂ 8	118.97	15.37	105.73	12.61	2.76
CaCl ₂ 2	156.99	53.39	138.54	45.42	7.97
CaCl ₂ 1	192.64	89.04	167.16	74.04	15.00
SrCl ₂ 8	118.36	14.76	105.77	12.65	2.11
SrCl ₂ 2	156.28	52.68	137.22	44.10	8.58
SrCl ₂ 1	192.35	88.75	167.29	74.17	14.58

DISCUSSION OF RESULTS.

The figures in the column marked "Increase over S of KCl" mean the increase in specific conductivity caused by the amount of the added salt in question, over the specific conductivity due entirely to the potassium salt. The figures in column marked "Increase over S of 0.6951m CaCl_2 " mean the same with reference to the solutions of calcium chloride, isochloric with the potassium chloride. The last column contains the difference between the values in the two columns just mentioned. It is to be noticed, in all the cases studied, that the increase in conductivity is greater in the case of the potassium chloride. The increase for the last three added salts is about the same. What does this mean?

The driving back of the dissociation, due to the anions of the isochloric solutions, is the same in both cases; a necessary consequence of the solutions being isochloric. Other things being equal, it would be expected that the increase in conductivity would be the same in the two solutions; since the conductivity is a measure of the dissociation. How can the above facts be explained?

We have a tentative explanation which is by no means final. When a salt is added to water or to the solution of another salt, the added salt is dissociated by the water present. We believe that the combined water, in the solution of hydrated salts, is less associated than the free water, in which case the added salts would be less dissociated; since the dissociation power of a solvent changes with its own association. And further, this effect would be greater the greater the concentration, since more combined water would then be present in the solution of calcium chloride. This seems to be in accord with the facts established.

These results and conclusions are to be regarded as preliminary. Viscosity undoubtedly plays a rôle, especially in the more concentrated solutions. The atomic volume and the velocities of the ions also must be taken into account.

Taking all of the factors into consideration, these results render highly probable the conclusion that the *dissociating power of combined water is less than that of uncombined water.*

In conclusion, we would thank Dr. E. J. Shaeffer, who, as the result of his spectroscopic investigations in this laboratory, suggested the study of this problem.

CHAPTER X.

THE ABSORPTION BY SOILS OF POTASSIUM FROM AQUEOUS SOLUTIONS OF POTASSIUM CHLORIDE.

By A. G. McCall, WITH THE COÖPERATION OF F. M. HILDEBRANDT, F. S. HOLMES,
E. S. JOHNSTON, AND S. F. TRELEASE.

As early as 1866 Frank¹ studied the retention of potassium chloride by the soil, using metal cylinders 3 inches in diameter and varying in length from 3 to 6 feet. His solution contained 1 gram of potassium chloride per liter of water. He found that the first foot of soil retained 91 per cent of the potassium chloride, while the first 18 inches removed 95.5 per cent of the salt. The solution appearing at the bottom of his 6-foot columns had lost all but 2 per cent of their original salt content. The addition of sodium chloride to the solution diminished the absorption of the potassium chloride.²

As the result of his experiments with potassium salts Treutler³ concluded that the deeper penetration of the potassium into the soil was to be secured by the use of potassium chloride rather than by the application of potassium sulphate as a fertilizer.

Peat and preparations of the humic acids were found by Heiden,⁴ to have the power of removing a part of the salt, when brought into contact with solutions of potassium chloride. The greater part of the salt was readily recovered by the use of a small quantity of water. Liebermann⁵ reported that aqueous solutions of potassium chloride showed no change as to acidity or alkalinity after passing through animal charcoal, but that the concentration was decreased.

More recent work on absorption has not only confirmed these earlier observations, but has brought out the fact that finely divided substances exercise a selective action with respect to the solutions with which they are brought in contact. In some cases the effect of this selective action is to remove one ion of the salt more rapidly than the other, leaving the solution acid or alkaline, depending upon which ion is absorbed to the greater extent. Cameron and Bell⁶ found that absorbent cotton has the power of removing the potassium ion from a solution of potassium chloride more rapidly than the chlorine, leaving the solution decidedly acid to ordinary indicators. Previous to this

¹Landw. Vers.-Stat., 8, 45 (1866).

²In this paper the terms "absorption" and "adsorption" are used, the former to denote the removal of material from solution regardless of whether the act is essentially chemical or physical, and the latter to designate the same process when the act appears to be clearly physical, that is, dependent upon the extent of surface alone.

³Landw. Vers.-Stat., 12, 184 (1869); 15, 371 (1872).

⁴Hoffman's Jahresb., 1866, p. 29.

⁵Wien. Akad. Ber., 74, 331 (1877).

⁶U. S. Dept. Agriculture, Bureau of Soils, Bulletin 30 (1905).

work, van Bemmelen¹ had shown that the treatment of a soil with a solution of potassium chloride resulted in an almost complete exchange of potassium for sodium, calcium, and magnesium. In one experiment he determined the chlorine and found that the amount had not changed.

Schreiner and Failyer² percolated a solution of potassium chloride through a short column of clay soil at the rate of 50 c.c. in 24 hours. The first few hundred cubic centimeters of the 200 parts per million solution, in passing through the soil, was reduced in concentration to approximately 60 parts per million of potassium. In the succeeding fractional percolates the concentration gradually increased until it reached 173 parts per million when 1,100 c.c. had passed. Up to this point the soil had retained approximately 900 parts per million of potassium. The absorption obtained with clay loam was less than that observed in the clay, while loam soil gave results intermediate between the clay and the clay loam. For the sandy loam used, the absorption was much less marked than in the finer textured soils, but was, nevertheless, quite marked in the first fractional filtrates. At the close of the absorption periods the clay and the clay loam soils were washed with distilled water, the percolation of water being at the same rate as that used in passing the potassium solution. After about 450 c.c. of water had passed through the clay soil the successive fractional percolates showed a practically constant composition of 20 parts per 1,000,000 of potassium. The washing was continued until over 2 liters of water had passed, at which time the quantity of absorbed potassium in the soil had been reduced to 350 parts per 1,000,000 from an initial concentration of 900 parts. With the clay loam the removal of the absorbed salt was more rapid. The quantity of potassium in this soil was reduced from 570 to 250 parts per 1,000,000 with the passing of approximately 800 c.c. of water.

Patton and Waggaman³ have recalculated the results of Peters's⁴ work on the absorption of potassium chloride from aqueous solutions by the soil. They bring out the fact that the absorptive effect is nearly twice as great with dilute solutions as with the strong concentrations. With his most dilute solution (1.011 grams of potassium per kilo of soil) 94 per cent of the total potassium present was absorbed, while from a solution 20 times as strong only about 55 per cent was removed.

In the same publication Patton and Waggaman call attention to the fact that the maximum absorptive capacity of an absorbent, while a perfectly definite quantity, is of little practical interest in soil studies, because of the fact that maximum absorption can take place only in the presence of a solution which is saturated with respect to the solute and at the same time is in equilibrium with the absorbing material.

¹Landw. Vers.-Stat., Bd. 21, pp. 135-191 (1877).

²U. S. Dept. Agriculture, Bureau of Soils, Bul. 32 (1906).

³*Ibid.*, Bul. 52, (1908).

⁴Landw., Vers.-Stat., 2, 129 (1860).

From a solution which is less than saturated, an absorbent can remove a quantity of the solute which is less than its maximum absorbent capacity, but which is, nevertheless, a definite amount for any particular concentration. They use this quantity as a measure of the specific absorptive capacity of the medium with respect to that particular solution. A solution of potassium chloride brought into contact with the soil will lose some of its potassium at a rate which gradually decreases until the salt reaches an equilibrium between the soil and the solution. The weight of potassium chloride absorbed by 1 gram of soil represents the specific absorptive capacity of the soil for that concentration of the salt at that particular temperature. If conditions in the soil are altered, more salt may be absorbed, or a part of the salt already absorbed may go back into solution. Thus it is seen that the absorption process is a reversible phenomenon.

In summarizing his recent work at the Bureau of Soils, Parker¹ states:

"The rate of adsorption of the chlorine ions from a solution by soils is much less than of potassium ions. The selective adsorption of potassium from a potassium chloride solution by a soil increases in amount with the concentration up to a certain point, and then remains practically constant. In general, the smaller the soil particles the greater the selective adsorption of the potassium from a potassium chloride solution by the soil."

Williams² has recently called attention to some special cases of selective adsorption to which he has given the name "negative adsorption." He cites the work of Gore³ as the first case of negative adsorption. He also calls attention to the work of Lagergren,⁴ who observed that, upon shaking solutions of electrolytes with charcoal or silica, the concentration of the salt solution *increased* instead of decreasing. Using blood charcoal, Williams found negative adsorption with potassium chloride at certain concentrations. Up to a concentration of 0.0563 gram of salt per gram of solution, the absorption was positive, becoming negative with further increase in concentration. Gore's work, cited above, gives instances of negative adsorption at low concentrations, becoming positive in less dilute solutions of the same salt. In all of the work cited the investigators have had their interest centered upon the condition of the solution after equilibrium had been reached; consequently, the solutions were left in contact with the absorbing medium for from 24 hours to several days. In the extensive studies made in the Bureau of Soils,⁵ United States Department of Agriculture, the contact time was usually a 24-hour period.

Throughout the work in which soils have been the absorbing medium, there exists a very great deal of uncertainty concerning the fundamental character of the phenomenon. The evidence from the use of chemi-

¹Journal of Agricultural Research, U. S. Dept. Agriculture, vol. 1, No. 3 (1913).

²Trans. Faraday Society, vol. x, part 1, Aug. 1914.

³Chemical News, 69, pp. 23, 33, and 44 (1894).

⁴Bihang till K. Svenska Vet-Akad. Handlingar, 24, II, 4 (1898).

⁵Bul. 32 (1906) and Bul. 52 (1908).

cally inert substances, such as charcoal and silica, would indicate that the process is a physical one, the magnitude of the adsorption depending upon the extent of the surface presented by the adsorbing medium. On the other hand, some of the very earliest work with soils gave strong evidence of the chemical replacement of the bases of the soil by the base contained in the solution. With these facts in mind a series of experiments were planned for the purpose of studying, (1) the effect of a short time contact between the soil and the salt solution; and (2) the effect of the extent of surface upon the amount and the rate of absorption.

In the following experiments a sample of Durham sandy loam¹ soil from Cabarrus County, North Carolina, was used as the absorbing medium and potassium chloride as the material absorbed. For the first series of experiments a sample of the soil was dried and passed through a 2 mm. sieve. For the second series, a sample of the same soil type was reduced to very fine condition by grinding for 4 days in a porcelain-lined ball mill. The mechanical analyses of the two samples, as made by the Bureau of Soils, United States Department of Agriculture, are given in table 96. It will be seen from the table that practically all of the sand has been reduced by the grinding to the silt and clay groups, thereby making an enormous increase in the amount of surface exposed by the two samples of what was otherwise identical material. The solution used was potassium chloride of approximately five-hundredth normal concentration.

TABLE 96.—*Mechanical analyses of soil samples.*

Soil.	Fine gravel, coarse sand, medium sand, 2.0 to 0.25 mm.	Fine sand, very fine sand, 0.25 to 0.05 mm.	Silt, 0.05 to 0.005 mm.	Clay, 0.005 to 0.0 mm.
Durham sandy loam:				
Natural soil.....	47.1	31.4	17.9	3.8
Pulverized four days in ball mill.....	0.5	9.7	78.1	12.0

DESCRIPTION OF THE APPARATUS.

In order to secure a short time contact between the soil and the solution a special apparatus was used, whereby the solution could be percolated through the soil at any desired rate. The apparatus consists of a porcelain-lined filter chamber A (fig. 17), into which is fitted a short filter tube B, made by cutting off the upper end of a Pasteur-Chamberland filter tube and forcing it down over the projection on the rubber gasket C. Surrounding the filter tube is a brass jacket D, which serves as a container for the soil. After the introduction of the soil, the solution is poured into the outer jacket, the air-tight cap E is

¹U. S. Bureau of Soils classification, Bul. 95, p. 32.

screwed down over the top of the filter chamber, and the system connected to an automobile-tire pump through the valve F. The filter tube serves to hold back the fine soil particles and give a clear filtrate for analysis. The apparatus is charged by putting 20 grams of the air-dry soil in the brass jacket surrounding the filter tube, and pouring the salt solution into the porcelain-lined chamber which surrounds the system.

SERIES 1.

Preliminary to the use of the soils for the absorption work, samples of both the natural and the finely pulverized soil were tested for soluble potassium, by percolating pure distilled water through them at the approximate rate of 200 c.c. per hour. Each successive 100 c.c. portion of the filtrate was saved and separate determinations made for potassium by the calorimetric method used by the Bureau of Soils.¹

Table 97 contains the results of this preliminary work. The numbers in the first column indicate the successive filtrates, while the second column gives the concentrations of the successive portions of the filtrate in parts per million of the solution. The figures of the table will be used in the subsequent work, in order to correct the results for the soluble potassium originally contained in the soil. Although it has no direct bearing upon the questions under consideration, it is of interest to note that the grinding of the soil in the ball mill has increased its solubility in distilled water approximately ten-fold.

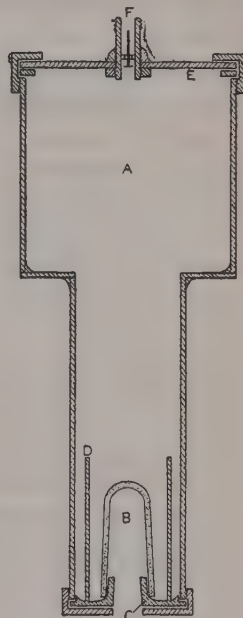


Fig. 17.

TABLE 97.—*Water-soluble potassium in samples of Durham sandy loam soil.*

Fractional filtrates.	Parts per million of potassium in filtrates.	
	Natural soil.	Pulverized 4 days in ball mill.
1	3.6	37.5
2	2.2	22.0
3	1.8	20.0
4	1.6	20.0

SERIES 2.

In this series a 20-gram sample of the same natural soil as was used in series 1 was percolated with 250 c.c. of a 0.005 solution of potassium chloride, the flow being maintained approximately at the rate of 50 c.c. in 10 minutes. The percolate was collected in fractions of 50 c.c. each,

¹U. S. Dept. Agriculture, Bureau of Soils, Bul. 31, p. 31.

and the potassium was determined calorimetrically. Immediately following the percolation with the solution of potassium chloride, pure distilled water was forced through the sample at the same rate in order to study the removal of the absorbed potassium. As a check upon the calorimetric determinations, the specific conductivity of the fractional filtrates was determined by measuring the conductivity of the solutions in a standardized Arrhenius cell, according to the method described by Jones.¹

TABLE 98.—*Absorption of potassium by a sandy loam soil, from a solution of potassium chloride containing 62 parts per million of potassium.*

Fractional filtrates.	Parts per million of potassium in the fractions.	Potassium retained in parts per million of dry soil.	Specific conductivity at 0°.
1	40	58	92
2	36	124	82
3	40	181	79
4	44	226	79
5	59	233	78

TABLE 99.—*The removal of the absorbed potassium by leaching with distilled water.*

Fractional filtrates.	Parts per million of potassium in the fractions.	Potassium retained in parts per million of dry soil.
1	7	214
2	11	186
3	9	165
4	9	142
5	9	118
6	8	99

It will be seen from table 98 that the first 10-minute contact of the solution with the soil reduced its concentration from 62 parts per million to 40 parts per million. At the end of the second 10 minute period the strength of the solution is further reduced to 36 parts per million, but from this point the concentration of the solution rises until the fifth and last fraction is reached, when the concentration is within 3 parts per 1,000,000 of the concentration of the original solution. The third column shows that the amount of potassium retained by the soil rises gradually to 233 parts per million of the dry soil, when 250 c.c. of solution has passed through.

Figures 18 and 19 represent graphically the results given in tables 98 and 99. In figure 18 are shown the results based upon the concentration of the successive fractional filtrates; the large curve representing the concentration in parts per million of potassium, and the small curve the specific conductivities. The curve for the potassium shows that the first three fractions of the filtrate are reduced approximately to two-thirds of the strength of the original solution. With the increase

¹Elements of Physical Chemistry, 4th edition, pp. 377 to 383.

in the volume of the filtrate the curve rises and almost reaches the upper boundary of the figure, which line represents the original strength of the solution. At this point the removal of the absorbed potassium is begun by leaching with pure distilled water. It should be noted that at this point the curve falls rapidly to practically a straight line.

Figure 19 gives the results expressed in terms of the soil, the abscissæ being the volume of the solution or water percolated through the soil, and the ordinates the amount of potassium absorbed, expressed in parts per million of the air-dry soil. While it is possible, and indeed quite probable that complete equilibrium was not reached, it is apparent

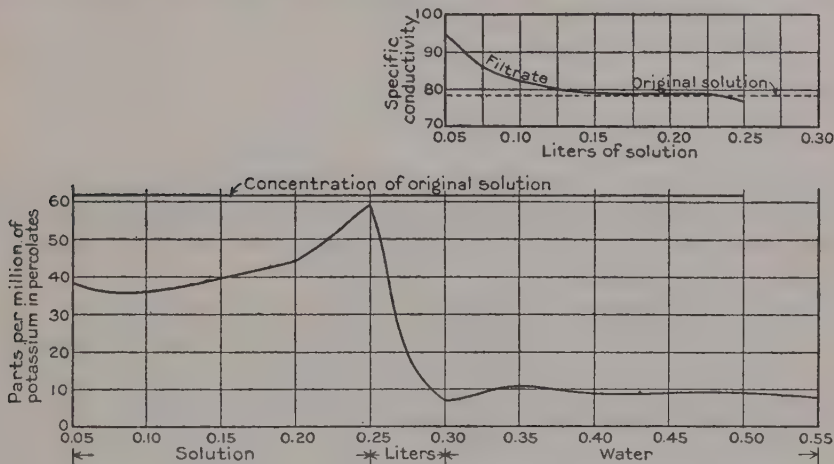


FIG. 18.

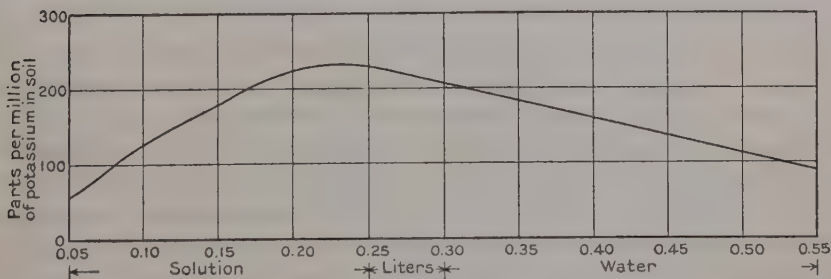


FIG. 19.

that the soil is rapidly approaching a saturated condition after having absorbed 230 parts per 1,000,000 of potassium as a result of the percolation of 250 c.c. of the salt solution. The part of the curve representing the removal of the absorbed salt by leaching with distilled water is a straight line, showing the uniformity with which the absorbed material is removed. This removal of the absorbed potassium was accomplished by filling the filter chamber with distilled water and continuing the percolation at the same rapid rate as was used with the solution of potassium salt.

SERIES 3.

For series 3, Durham sandy loam, pulverized four days in a ball mill, was used. The manipulation was the same as for series 2, except that the fractional percolates were 100 c.c. instead of 50 as in the previous

TABLE 100.—*Absorption of potassium solution by a finely pulverized sandy loam from a solution of potassium chloride containing 78 parts per million of potassium.*

Fractional filtrates.	Parts per million of potassium in the fractions.		Specific conductivity of solutions at 0°.
	Original determinations.	After correction for water-soluble potassium.	
1	144	107	112
2	112	91	82
3	100	82	82
4	112	92	84

series, making the total volume of the solution twice as great. An inspection of table 100 brings out the surprising fact that the amount of potassium in the solution has been *increased* instead of decreased by its contact with the soil.

A part of this increase in concentration is undoubtedly due to the fact that the pulverized soil has given up some of its potassium to the percolating solution. However, this is not

TABLE 101.—*Removal of absorbed potassium by leaching with distilled water.*

Fractional filtrates.	Parts per million of potassium in the fractions.
1	39
2	24
3	21
4	18
5	15
6	18

sufficient to account for all of the increase in potassium content. In column 3 of table 100 is given the potassium in the fractional percolates, after they have been corrected for the water-soluble potassium of the soil. This correction is based upon the assumption that pure water in contact with the soil will dissolve potassium at the same rate, and in the same amounts as the very dilute solution of potassium chloride used in these experiments.

Proceeding upon this assumption, pure water was percolated through the sample of pulverized soil, and the amount removed by the water was applied as a correction to the corresponding fractional percolates of the salt solution.

The results given in table 100 are shown graphically by the curves in figure 21. The dotted line forming the upper arm of the curve represents the original concentration of the successive fractions, while the solid line represents the strength of the solutions after the correction has been applied. It will be seen that, even after the correction has been made, the solution still maintains a concentration higher than the original salt solution. This appears to be a case of selective absorption, in which the solvent (water) is absorbed more rapidly than the dissolved

potassium salt, with the result that the percolate is more concentrated than the original solution. It should be borne in mind, however, that we are probably not dealing with equilibrium conditions. The mechanism by which this negative absorption is effected, may be explained by assuming that the solvent and the dissolved substance are capable of being absorbed more or less independently and at different rates. The rapid advance of the liquid through the fine pores of the soil results, for a time, in the more rapid absorption of the water than of the salt,

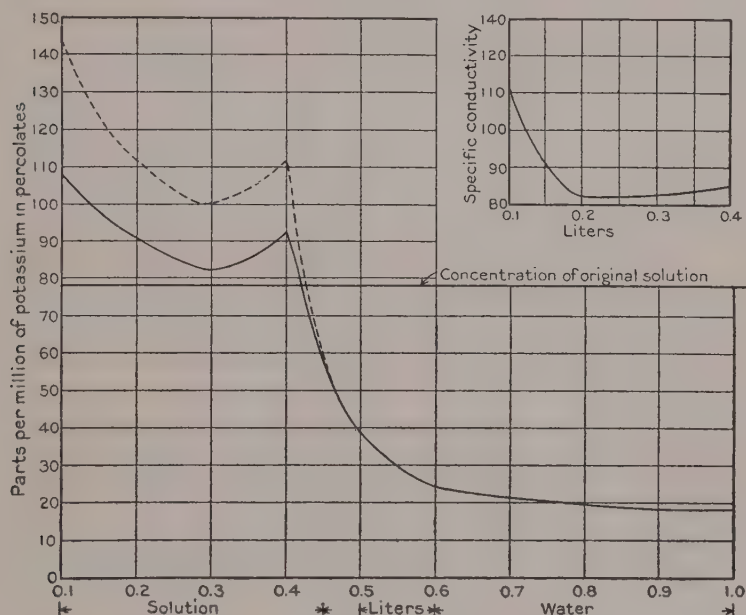


FIG. 21.

leaving the liquid in the larger non-capillary spaces more concentrated. This more concentrated solution then moves through the large spaces and appears as the percolate. It is quite probable that after a few hundred cubic centimeters have passed through, equilibrium will have been established and the negative absorption will become positive. This so-called negative absorption, therefore, may be considered as a special case of selective absorption.

From the work of Williams, to which reference has been made, it appears that the absorption of the solute and the solvent is dependent upon the relative masses present. With some electrolytes in water it has been found experimentally that the absorption is at first positive, increases to a maximum, decreases through zero, and finally becomes negative, but there seems to be no case on record in which the initial absorption effect is negative.



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